Heat Capacity of Gaseous Carbon Dioxide [1]

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The heat capacity (C_p) of gaseous carbon dioxide has been measured at $-30°$, $0°$, $+50°$, and $+90°$ C and at 0.5-, 1.0-, and 1.5-atmosphere pressure, with an accuracy of 0.1 percent. The flow calorimeter used was a modification of the one previously described by Scott and Mellors [1] [2] and Wacker, Cheney, and Scott [2]. In order to test the accuracy of the calorimeter, the heat capacity of oxygen was measured at 1 atmosphere at $-30°$, $0°$, and $+50°$C. The measured values of C_p for oxygen were combined with an equation of state to give C_p°; these differed from the statistically calculated values by $+0.03$, -0.06 and -0.01 percent at the three temperatures.

The experimental values of C_p for carbon dioxide have been used to calculate new values of C_p° and values of the pressure coefficient of heat capacity at the four temperatures of measurement. The theoretical values of C_p° calculated in 1949 [8] were found to be too low by 0.2 to 0.3 percent; the results of a new calculation are in substantial agreement with the experiments. The pressure coefficients are in agreement with those obtained from the recent pressure-volume-temperature work of MacCormack and Schneider [7].

1. Introduction

The large number of experimental values of the specific heat of carbon dioxide reported in the literature are in serious disagreement with each other. Leduc, for the International Critical Tables [3], attempted to evaluate and correlate all of the work, both experimental and theoretical, up to 1929. It is now thought that these ICT values are in considerable error. There have been two calorimetric measurements of the heat capacity since that time [4, 5]. There have also been at least two good sets of pressure-volume-temperature measurements [6, 7] and two calculations of the ideal gas heat capacity from spectroscopic data [8, 9]. There have been several compilations, based almost entirely on the combination of equations of state with spectroscopic values of C_p° [10 to 13]. Values from several sources of the heat capacity in dimensionless units, C_p/R, at 1 atmosphere and $0°$ C, are given here.

Partington and Schilling, 1924 [14]	4. 40
Leduc, ICT 1929 [3]	4. 37
Eucken and v. Lude, 1929 [4]	4. 348
Sweigert, Weber and Allen, 1946 [10]	4. 487
NBS–NACA Table 13.24, 1949 [12]	4. 396
MacCormack and Schneider, 1950 [13]	4. 363

The present investigation was undertaken because of the impossibility of deciding which values to choose and because of the reluctance, on the part of some users of thermodynamic tables, to accept statistically calculated values without supporting experimental evidence.

Oxygen was chosen as a substance to test the accuracy of the apparatus, because its heat capacity is well known and because a pure sample is rather easily prepared.

2. Materials

The oxygen was prepared by heating potassium permanganate as described by Scott [15] and by Hoge [16]. This is a method that has been shown to produce very pure oxygen. The vapor pressure of the sample at the temperature of boiling nitrogen was found to agree with the value calculated from Hoge's data [16]. During the course of the last series of measurements (those at $-30°$ C), a small air leak in the apparatus was suspected. As soon as the measurements were completed, a portion of the sample was dissolved in alkaline pyrogallol to determine the purity; the amount of residual gas was 0.2 percent, and it was assumed to be nitrogen from air that had leaked in.

Carbon dioxide was purified from commercial gas that had been made from limestone. A large cylinder containing 20 lb of carbon dioxide was opened and the gas allowed to escape until less than half of the contents remained. Several hundred grams were then transferred to a small evacuated cylinder, which was then attached to a purification train. The sample was slowly sublimed from the cylinder and condensed in a glass trap at liquid N_2 temperature, while a high vacuum was maintained by pumping on the trap. Transfer to the final receiver was also accomplished by sublimation and condensation. About 600 g were prepared in this way. The sample was tested several times for permanent gases by dissolving portions in concentrated potassium hydroxide and observing the volumes of residual gas. These were always less than 0.01 percent of the volume of the sample. A test performed by E. R. Weaver showed less than 0.001 percent of moisture.

3. Apparatus

The adiabatic flow calorimeter used in this work was a modification of one that was shown by Wacker, Cheney, and Scott [2] to give heat capacities reliable to better than 0.1 percent. The principal modifi-

cation was the substitution of two resistance thermometers of nickel wire for the thermocouple previously used for measuring the rise in temperature of the heated gas. The main advantage of this substitution was that the thermometers could be calibrated in place at any time. A further advantage was that it could be demonstrated by the readings of the lower thermometer that the gas entering the calorimeter always reached the temperature of the bath, and that there was negligible heat leak "upstream" from the hot calorimeter to the incoming cold gas.

The flow calorimeter, as it was used, is shown in figure 1. Most of the essential features are as described by Scott, et al. [1, 2], but so many changes have been introduced that a brief description of the entire apparatus appears desirable.
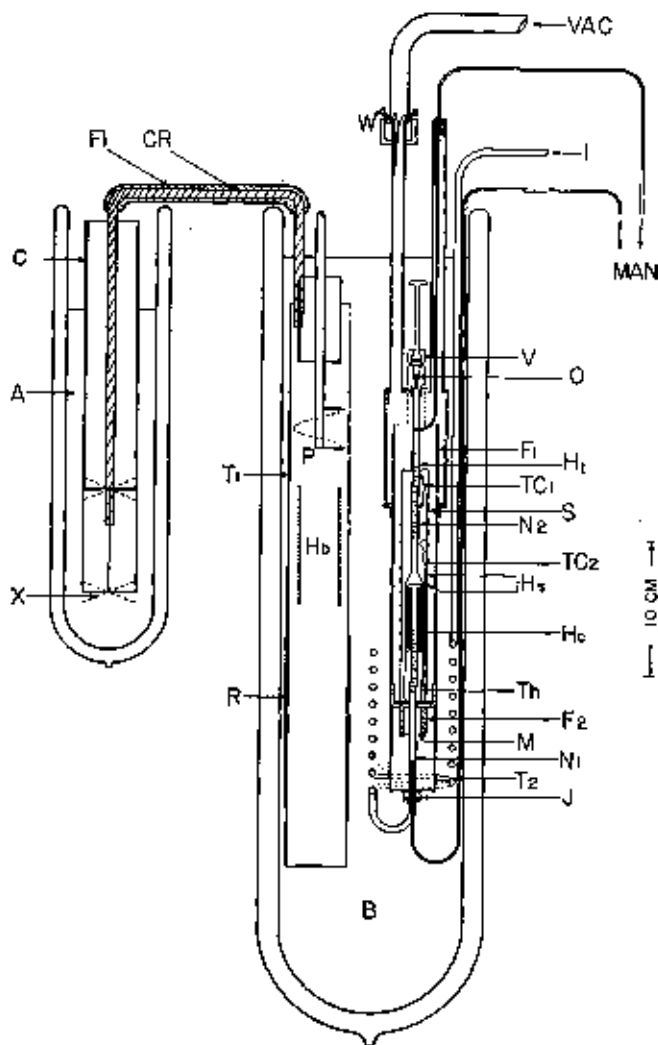

FIGURE 1. *Scale drawing of flow calorimeter.*

A, Liquid nitrogen; B, constant-temperature bath; C, protecting cylinder; CR, copper rod; F₁ and F₂, flanges; FI, felt insulation; Hᵦ, bath heater; Hₐ, calorimeter heater; Hₛ, shield heater; Hₜ, tube heater; I, inlet; J, bellows seal; M, mica spacer; MAN, manometer tubes; N₁ and N₂, nickel thermometers; O, outlet; P, propeller; R, bath-control thermometer; S, radiation shield; T₁, stirrer tube; T₂, helical tube; TC₁, tube thermel; TC₂, shield thermel; Th, metal thimble; V, throttle valve; VAC, vacuum line; W, wax seal; X, vanes.

3.1. Constant-Temperature Bath

The calorimeter is immersed in the bath, B, the temperature of which was controlled by supplying electric power to the heater, H_b. The stirring propeller, P, forced liquid down the brass tube, T_1, and over the copper resistance thermometer, R, which consisted of about 140 ohms of No. 37 AWG wire and which formed one arm of a Wheatstone bridge. An unbalance in the bridge circuit of 1 μv corresponded approximately to 0.001 deg K. The circuit was ordinarily attached to the galvanometer in a Rubicon phototube amplifier, the output of which was fed to a proportionating heat-control amplifier developed by the Electronic Instrumentation Section of the Bureau. This arrangement gave automatic control of the bath temperature within 0.002 deg, provided there were no large disturbances. The copper thermometer bridge could be switched from the controlling galvanometer to a sensitive wall galvanometer for manual control, or the two galvanometers could be placed in series for momentary observation of the efficiency of control.

When controlling the bath below room temperature, refrigeration was required, and this was provided by the apparatus shown at the left of figure 1. A solid copper rod, CR, with copper vanes, X, at one end and a copper cylinder at the other was immersed in liquid nitrogen, A. The metal tube, C, closed at the bottom end made the rate of heat transfer almost independent of the depth of the nitrogen in the dewar.

The bath liquid was a special light machine oil for temperatures above that of the room and an equivolume mixture of chloroform and carbon tetrachloride for temperatures below that of the room.

3.2 Flow Control

The source of gas flowing into the calorimeter is not shown in figure 1. For oxygen, this was a cylindrical brass boiler with heavy-copper vanes, wound with a heater and immersed in a cold dewar. The rate of flow was controlled by the power supplied to the heater on the boiler for evaporating the liquid oxygen. For carbon dioxide the boiler was replaced by a high-pressure system in which the carbon dioxide was contained in a steel cylinder immersed in melting ice. The pressure (34.38 atm) remained sufficiently constant for good flow control. The gas was admitted to the calorimeter, and its flow rate was controlled, by a very sensitive diaphragm valve. This valve was previously used by Osborne, Stimson, and Ginnings [17] for control of flow of high-pressure water. A silver seat moving down against a stainless steel crater-rim cone with a very small opening provided the closing action.

Both the rate of flow and the mean pressure during an experiment were adjusted, controlled, and measured by following the readings of a three-column manometer, two columns of which were connected to the calorimeter as shown in figure 1, whereas the third was open to the atmosphere.

3.3 Calorimeter and Shield

The gas being investigated entered at I and passed through the helical tube, T_2, where it was brought to the temperature of the bath. This tube passes into the vacuum jacket through the bellows joint, J, which was intended to prevent stresses caused by differential expansion.

The calorimeter, considered as the vertical tube between points J and O through which the gas flowed, was constructed of thin-walled seamless Monel tubing. The various pieces were soldered together as nearly coaxially as possible, and the whole length was supported only at the two ends, and at M by a mica spacer. The copper thimble, Th, was used to provide a surface of higher temperature to protect the incoming cold gas from radiation; it was thermally a part of the calorimeter. The latter, with the exception of the necessary lead wires, was completely isolated from contact with surroundings from points M to O. The thimble was gold-plated and polished; the Monel tubing was covered with thin aluminum foil, except for a short length that was highly polished. The copper radiation shield, S, was gold-plated and polished on the inside, and covered with aluminum foil on the outside. It was supported and centered by string spacers.

The temperature of the gas entering the calorimeter was measured by the nickel resistance thermometer, N_1; the gas passed over a system of baffles and went twice past the glass-silicone-insulated No. 36 AWG constantan heater, H_c. The direction of flow was again reversed, and another system of baffles was encountered in the region where the exit temperature was measured with the nickel resistance thermometer, N_2. Heat leak to the upper tube was opposed by supplying heat to a tube heater, H_t, so that zero temperature gradient was maintained as indicated by a null reading of the copper-constantan thermocouple, TC_1. Radiation to or from the outer surface of the calorimeter was reduced almost to zero by heating the shield with the heaters, H_s, which were so arranged that any desired proportion of the heat could be supplied to the top half of the shield. The three junctions of the chromel-constantan thermocouple, TC_2, could be read in summation or individually, and the attempt was made to keep all of the readings near zero. Heat transfer from the bath by gas conduction was eliminated by evacuating the brass jacket.

Leads were brought in through the wax seal, W, and were tempered nearly to bath temperature on the brass cylinder, F_1. Leads from the thermometer, N_1, were taken directly to the brass ring, F_2, and further tempered; all other leads were wound twice around the shield. All leads were of AWG No. 34 copper wire, silk-and-enamel insulated. All wires, whether heaters, thermometers, thermal junctions, or leads, were cemented to the metal surfaces with glyptal lacquer and afterward baked.

Each nickel thermometer consists of about 55 ohms of AWG No. 40 enameled nickel wire with four copper leads. The thermometers were calibrated by comparing with one or more platinum resistance thermometers suspended in the bath when helium was in the calorimeter jacket. It was found that the resistance of the nickel thermometers in use fluctuated slowly over a range corresponding to 3 or 4 mdeg during a period of 3 months. Consequently, spot checks of the calibration were made each day of heat-capacity measurements.

After leaving the calorimeter through the throttle valve, V, the gas went to one or the other of two receivers through a snap-throw valve, capable of changing the flow from one receiver to the other in less than 0.1 second. This valve in one of the two positions closed the clutch circuit of an interval timer that was driven by a special constant-frequency 60-cycle current, accurate to 0.02 second. This valve was the same one described by Wacker, Cheney, and Scott [2]. The receivers were kept at the temperature of liquid nitrogen.

A Leeds & Northrup G-2 Mueller bridge was used to measure resistances. The potential and current in the calorimeter heater were measured with a precision potentiometer, in conjunction with a calibrated standard resistor and a calibrated volt box. The circuits were essentially the same as those described by Scott, Meyers, Rands, Brickwedde, and Bekkedahl [18].

4. Method

The selection of the temperatures and pressures at which to measure the heat capacity of carbon dioxide was made to cover the working range of the calorimeter and obtain as many points as necessary. The usual assumption was made, that the error in an apparent heat capacity caused by heat leak would be inversely proportional to the flow rate. Consequently, at each temperature and pressure, a number of determinations were made over as wide a range of flow rates as was consistent with a reasonable time for measurement, with the size of sample, or with the capacity of the calorimeter.

The determinations of the heat capacity included the measurements necessary to obtain the three fundamental quantities: the mass rate of flow, F, of the gas through the calorimeter; the electric power, W, to the calorimeter heater; and the rise in temperature of the gas, ΔT.

A heat-capacity experiment was begun by adjusting both the valve, V, and the flow of gas to the calorimeter until the selected values for the mean pressure and pressure drop were obtained. Meanwhile, power was supplied to the heater and adjusted. Neither valve V nor the power supply were changed after the initial adjustment, all control being at the source of gas. Heat was also supplied to the shields. After a length of time that was inversely proportional to the rate of flow, a steady state was reached in which the heated portion of the calorimeter and the shield were at a constant temperature that was approximately 10 deg higher than the constant bath temperature. At this time the gas was directed by means of the snap-throw valve to the other (weighed) receiver, thus starting the measurement. Contin-

uous measurements of the exit temperature (N_2) of the gas were made, and slight adjustments of the flow were made to keep that temperature constant within 0.03 deg. In addition to the measurements of the resistance of the thermometer, N_2, readings of current and potential of the heater, resistance of N_1 and the bath thermometer, and heights of the three mercury columns were recorded as often as possible in connection with each run. When about the desired weight of sample had been collected and the temperature was nearly constant and the same as that at the start of the run, the experiment was terminated and the gas was redirected to the other container. The barometric pressure was also recorded, as well as the reading of the interval timer. The receiver was weighed on a large analytical balance, and the weight of sample was corrected for buoyancy.

"Blank" experiments were required in which the temperature drop, δT, in the calorimeter was measured when no heat was applied. This temperature drop is chiefly due to Joule-Thomson cooling, but heat leaks and responsiveness of the nickel thermometers to the gas temperature usually contribute. The blank experiments were made with the bath temperature approximately at the mean temperature of the corresponding heat-capacity measurements, and they were made at the same mean pressures and over the same range of pressure drops as the heat-capacity experiments. The values of $\delta T/\Delta p$ were plotted as a function of Δp for each pressure

and temperature for each gas. These graphs were used to obtain the quantity δT for each heat-capacity experiment. The value of δT varied from 0.005° to 0.4° in the extreme cases.

The apparent specific heat of the gas, C, at the mean temperature and pressure of the experiment was computed by the relation

$$C = \frac{WF^{-1}}{(\Delta T + \delta T)}. \tag{1}$$

The mean temperature, T_m, of the experiment was calculated as the bath temperature plus $\Delta T/2$. The average pressure, p_m, in the region of the calorimeter between the thermometers N_1 and N_2 was calculated, from the corrected manometer and barometer readings, as equal to the pressure at the entrance to the calorimeter minus three-eighths of the measured pressure drop, Δp. A consideration of the geometry of the calorimeter had led the authors to the opinion that the factor three-eighths is near the truth and that any uncertainty in this factor will not affect the result by a significant amount.

5. Results

5.1 Tests with Oxygen

All the heat-capacity data on oxygen from this investigation are given in table 1. The experiments

TABLE I. *Data on oxygen*

Reciprocal of rate, F^{-1}	Mass of sample, m	Power, W	Pressure drop, Δp	Temperature rise, ΔT	Blank correction, δT	Heat capacity, C*	Correction for T_m and p_m, δC	Heat capacity, C_p (observed)
			−30.00° C = 243.16° K; 1.00 atm					
sec. g⁻¹	*g*	*Watt*	*mm Hg*	*°K*	*°K*	*jg⁻¹ deg⁻¹*	*jg⁻¹ deg⁻¹*	*jg⁻¹ deg⁻¹*
11.9673	70.7708	0.762695	220.7	9.8817	0.0965	0.91480	−0.00012	0.91477
20.1029	49.0120	.467512	97.5	10.0141	.0382	.91487	−.00006	.91481
24.2569	41.8857	.381375	67.4	10.0887	.0271	.91488	−.00004	.91484
37.9689	26.9076	.340604	27.8	9.9815	.0141	.91435	−.00002	.91438
44.7508	20.0441	.208395	20.2	9.9464	.0096	.91419	−.00004	.91415
Extrapolated value								0.91519
			0.00° C = 273.16° K; 1.00 atm					
11.1876	60.7721	0.798101	357.4	9.5978	0.1222	0.91604	−0.00008	0.91616
11.5440	99.1040	.781965	334.4	9.7391	.1157	.91606	−.00009	.91597
11.5257	79.9103	.790840	320.9	10.1718	.1117	.91608	−.00011	.91597
11.8486	62.8561	.796898	320.0	10.1910	.1115	.91632	−.00010	.91623
19.1670	27.8817	.420780	125.0	8.7491	.0501	.91646	−.00013	.91633
19.7966	68.4814	.413786	114.2	9.0000	.0462	.91639	−.00004	.91635
24.9897	33.1234	.344969	73.2	9.3736	.0311	.91655	+.00002	.91657
35.0715	26.4082	.232635	36.5	8.8815	.0177	.91629	.00000	.91629
37.2491	28.4235	.232170	33.2	8.4206	.0173	.91619	+.00002	.91621
46.1158	30.2536	.109647	22.2	9.6852	.0156	.91571	+.00001	.91572
Extrapolated value								0.91626
			50.00° C = 323.16° K; 1.00 atm					
11.9923	111.6318	0.667217	297.3	11.1740	0.0887	0.92327	−0.00020	0.92317
12.1809	46.6498	.666257	284.7	11.3270	.0846	.92305	−.00023	.92282
23.6091	24.1352	.442683	79.1	11.3069	.0233	.92272	−.00018	.92254
31.9923	23.4676	.279145	43.3	9.8740	.0129	.92191	−.00002	.92169
41.8940	23.4898	.226012	26.0	10.2856	.0077	.92152	−.00007	.92145
Extrapolated value								0.92366

* The values of C are corrected for 0.0035 g of oxygen left in the delivery tubes because of the vapor pressure of oxygen at the temperature of boiling nitrogen.

are listed in the order of decreasing flow rate at each temperature. The values of C, given in column 7, are calculated by means of eq 1. These are adjusted by the amounts given in column 8, to correct for the difference between T_m and the nominal temperature and between p_m and 1-atm pressure, and there are obtained the values of C_p (observed) in column 9. The values of C_p (observed) are plotted as a function of F^{-1}. The straight line drawn through the points was determined by the method of least squares, and the value of C_p is obtained as the intercept. One of these plots is shown in figure 2, to illustrate the precision obtained. The values of C_p obtained by this process are labeled "Extrapolated value" in column 9 of table 1. These values, converted to dimensionless form, C_p/R, are listed again in table 3 (a). There are also given the corrections to ideality calculated by the Beattie-Bridgeman equation [19], and the resulting values of C_p°/R. These values are then compared with the values calculated by Woolley [20, 21] from the spectroscopic and molecular data.

5.2 Heat Capacity of Carbon Dioxide

All of the heat-capacity data on carbon dioxide in this research are given in table 2. In addition, plots of all the experimental results at -30° and $+50^\circ$ C are furnished in figures 3 and 4 to show the typical appearance of these plots and to indicate the precision. The value of C_p (observed) for each point (col. 9), after adjusting for the differences between T_m and p_m and the nominal temperature and pressure (col. 8), is plotted against the reciprocal of flow rate (col. 1). The slopes and intercepts of the lines were first obtained by the method of least squares. As the heat leak, of which the slopes of these lines is a measure, would be expected to be independent of pressure, the three lines at each of the temperatures except 90° C were adjusted slightly to a constant average slope. A small but regular change of slope with pressure was noted at 90° C, and these lines were therefore unchanged from the least-square values. The intercepts of these lines are the desired values of C_p and are listed in column 9 of table 2 as the "Extrapolated value." In order to furnish an estimate of the precision of these values of C_p, they are followed in table 2 by values of σ, where σ is defined as $\sqrt{\sum d^2/(n-1)}$, and d is the deviation from the extrapolated value of C_p, of each C_p (observed), after correcting for heat leak by use of the slope of the straight line previously found.

The values of C_p have been converted to dimensionless form and are given as C_p/R in table 3 (b). Although there are a number of experimental measurements at atmospheric pressure recorded in the literature, there is no interest other than historical in making comparisons with the very old work. Partington and Shilling [14], Leduc [3], and Quinn and Jones [22] have made studies that may be referred to. The most recent thermal measurements are those made by Kistiakowsky and Rice [5] by the isentropic expansion method. The values
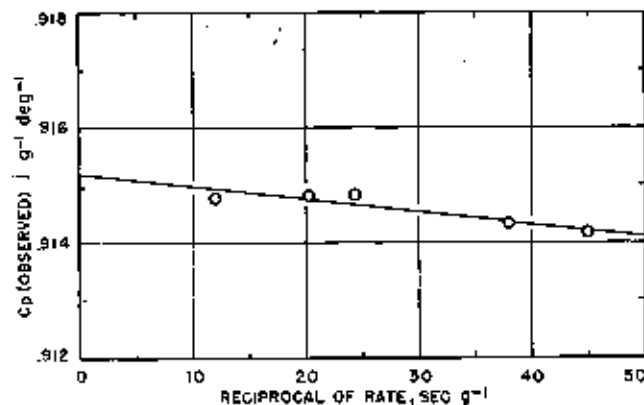

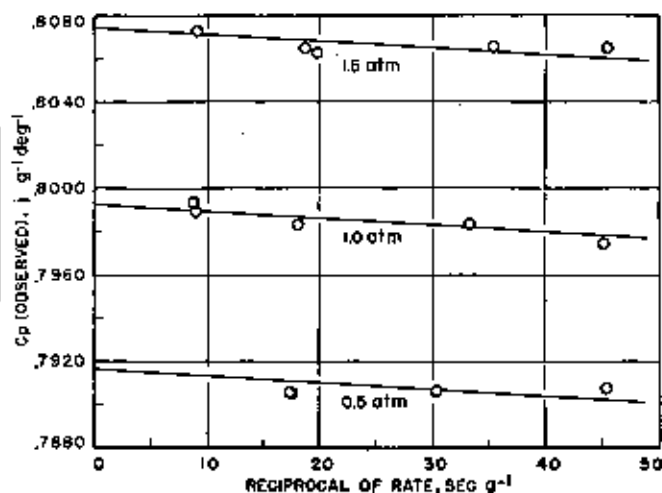FIGURE 2. *Heat capacity of oxygen at -90° C and 1 atmosphere.*

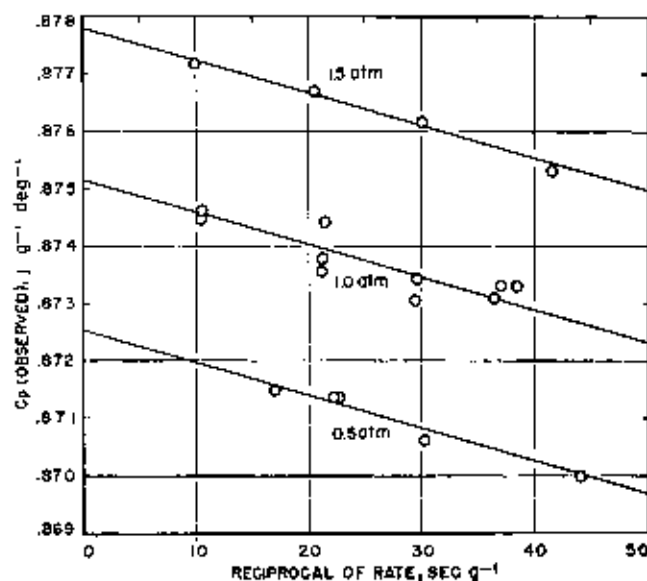FIGURE 3. *Heat capacity of carbon dioxide at -30° C and three pressures.*

FIGURE 4. *Heat capacity of carbon dioxide at 50° C and three pressures.*

TABLE 2. *Data on carbon dioxide.*

Reciprocal of rate, F^{-1}	Mass of sample, m	Power, W	Pressure drop, Δp	Temperature rise, ΔT	Blank correction, dT	Heat capacity, C	Correction for T_m and p_m, dC	Heat capacity, C_p (observed)
$sec\ g^{-1}$	g	$Watt$	$mm\ Hg$	$°K$	$°K$	$jg^{-1}\ deg^{-1}$	$jg^{-1}\ deg^{-1}$	$jg^{-1}\ deg^{-1}$
−30.00°C = 243.16°K; 1.50 atm								
3.8529	41.3700	0.383700	232.0	9.4287	0.2690	0.80772	−0.00044	0.90728
18.5247	38.6799	.483207	54.0	11.0151	.0740	.80721	−.00068	.90653
19.5828	40.5411	.470045	48.5	11.3377	.0674	.80708	−.00090	.80629
35.2678	27.3805	.238239	15.2	10.3697	.0230	.80699	−.00036	.90653
45.6761	37.3852	.171082	9.0	9.6685	.0181	.80548	−.00006	.90642
							Extrapolated value	0.90742
							σ	±0.00040
1.00 atm								
8.7592	90.6254	0.384995	360.7	9.2865	0.4018	0.79995	−0.00056	0.79939
8.9149	56.0436	.373842	343.2	9.3380	.3843	.79963	−.00067	.79896
17.9671	34.4900	.472573	85.3	10.5263	.1148	.79898	−.00064	.79834
33.1964	30.2534	.237875	25.9	9.5478	.0393	.79844	−.00007	.79837
44.5014	27.7185	.179918	14.1	10.0914	.0363	.79775	−.00035	.79760
							Extrapolated value	0.79925
							σ	±0.00032
0.50 atm								
17.2954	33.0664	0.471766	191.2	10.0749	0.2390	0.79111	−0.00044	0.79067
17.4890	33.8618	.469663	186.4	10.1265	.2340	.79107	−.00049	.79058
30.0816	13.5576	.268529	63.9	10.1155	.0928	.79076	−.00014	.79062
45.2457	25.3510	.169161	29.9	9.6347	.0459	.79055	+.00019	.79074
							Extrapolated value	0.79162
							σ	±0.00049
0.00° C = 273.16° K; 1.50 atm								
9.3013	57.1123	0.866416	201.4	9.5445	0.1454	0.83167	−0.00016	0.83151
9.3372	65.0724	.891963	233.6	9.8041	.2032	.83207	−.00040	.83167
9.3829	82.0585	.891606	233.4	9.7189	.2030	.83184	−.00035	.83149
9.5304	63.5383	.866533	191.6	9.7897	.1363	.83191	−.00035	.83156
18.0472	31.1528	.461388	54.1	9.9729	.0455	.83115	−.00022	.83093
18.4196	31.9291	.470372	60.9	10.3594	.0610	.83145	−.00049	.83096
18.5104	70.0752	.461507	51.5	10.2334	.0436	.83125	−.00036	.83089
18.5114	39.8585	.470640	60.6	10.4163	.0607	.83155	−.00041	.83114
19.0150	52.3550	.460423	49.4	10.4888	.0420	.83137	−.00032	.83105
27.9321	45.1789	.279317	22.0	9.3786	.0223	.83009	+.00005	.83004
33.2601	35.2783	.231057	19.3	9.2871	.0207	.83060	+.00044	.83074
33.2900	28.2507	.231259	19.4	9.2458	.0205	.83101	+.00013	.83114
36.3004	20.1507	.197887	13.9	8.6471	.0160	.82919	+.00048	.82967
36.9328	26.7567	.197941	13.6	8.7985	.0157	.82940	+.00047	.82987
44.0597	23.7891	.170483	11.0	9.0283	.0130	.83088	+.00011	.83099
52.5659	29.4592	.142725	7.0	9.0379	.0006	.82923	+.00043	.82966
							Extrapolated value	0.83178
							σ	±0.00042
1.00 atm								
9.7651	76.8902	0.664572	288.1	10.0045	0.2132	0.82636	−0.00016	0.82620
19.1194	30.6709	.438485	72.7	10.0663	.0640	.82585	−.00031	.82554
19.4948	29.6885	.439721	69.7	10.3133	.0637	.82606	−.00028	.82582
19.6780	31.9056	.440499	68.2	10.4224	.0594	.82663	−.00057	.82806
26.8229	40.7968	.279254	37.6	9.6375	.0398	.82518	+.00039	.82557
27.3293	21.1385	.280370	35.7	9.2462	.0392	.82520	+.00027	.82547
28.7456	30.6543	.278591	32.2	9.6719	.0359	.82510	−.00017	.83493
29.5021	23.1130	.279038	31.0	9.9595	.0334	.82546	−.00002	.82544
38.6255	21.0078	.228050	18.3	10.2730	.0956	.82537	−.00040	.82497
49.6069	29.4923	.154452	11.0	9.2763	.0197	.82430	+.00030	.82460
							Extrapolated value	0.82657
							σ	±0.00029
0.50 atm								
16.0773	55.3168	0.524271	226.5	10.0779	0.1857	0.82124	−0.00019	0.82105
20.7110	39.0001	.410999	129.2	10.2406	.1163	.82189	−.00037	.82152
20.8485	37.4840	.408322	128.3	10.2415	.1155	.82195	−.00033	.82162
26.7300	36.5463	.279879	77.6	9.0390	.0776	.82061	+.00030	.82091
27.0941	19.9896	.321392	78.8	10.5239	.0738	.82165	−.00059	.82106
38.8621	26.1406	.218921	36.3	10.3228	.0399	.83107	−.00047	.83060
39.4649	24.1511	.219413	35.3	10.5001	.0378	.82173	−.00054	.82119
51.4968	27.4080	.142701	21.2	8.0446	.0233	.81978	+.00028	.82006
							Extrapolated value	0.82196
							σ	±0.00029

TABLE 2. *Data on carbon dioxide*—Continued

Reciprocal of rate, F^{-1}	Mass of sample, m	Power, W	Pressure drop, Δp	Temperature rise, ΔT	Blank correction, tT	Heat capacity, C	Correction for T_m and p_m, δC	Heat capacity, C_p (observed)
sec g⁻¹	*g*	*Watt*	*mm Hg*	*° K*	*° K*	*jg⁻¹ deg⁻¹*	*jg⁻¹ deg⁻¹*	*jg⁻¹ deg⁻¹*

50.00° C =323.16° K; 1.50 atm

9.9533	62.1153	0.565713	201.7	9.7182	0.1036	0.87791	−0.00012	0.87719
20.5448	32.9410	.440265	49.0	10.2884	.0260	.87694	−.00024	.87670
20.0909	25.6935	.279579	23.4	9.5905	.0124	.87607	+.00010	.87617
41.6764	22.0562	.198506	12.5	9.4465	.0087	.87513	+.00018	.87531

Extrapolated value 0.87779
σ ..... ±0.00010

1.00 atm

10.4374	53.9567	0.866111	261.8	10.1896	0.1437	0.87484	−0.00037	0.87447
10.4894	73.2380	.868896	285.6	10.2484	.1453	.87488	−.00026	.87462
21.0786	40.0728	.447243	69.2	10.7445	.0877	.87434	−.00056	.87378
21.0995	25.2869	.445427	69.4	10.7141	.0379	.87410	−.00054	.87366
21.4479	37.7110	.406496	67.0	9.9321	.0366	.87469	−.00018	.87441
29.2761	21.0018	.290525	36.6	9.3590	.0202	.87298	+.00012	.87305
29.4729	32.2099	.290078	36.0	9.4321	.0193	.87333	+.00010	.87343
36.3511	25.2596	.226390	24.0	9.4134	.0133	.87300	+.00008	.87308
37.0996	28.1755	.234775	23.0	9.9595	.0123	.87347	−.00016	.87331
38.3836	27.9002	.219624	21.7	9.6411	.0120	.87329	+.00001	.87330

Extrapolated value 0.87515
σ ..... ±0.00030

0.50 atm

16.9244	33.9652	0.552830	232.6	10.0336	0.1375	0.87164	−0.00014	0.87160
22.0571	27.8684	.402422	131.4	10.1132	.0946	.87159	−.00023	.87136
22.5081	34.2599	.440823	125.3	11.3464	.0801	.87220	−.00083	.87137
30.2390	34.4858	.279988	69.9	9.6780	.0465	.87064	−.00001	.87063
44.1108	23.2882	.216601	33.7	10.9518	.0230	.87058	−.00060	.86998

Extrapolated value 0.87251
σ ..... ±0.00012

90.00° C=363.16° K; 1.50 atm

10.6379	53.2143	0.865606	199.9	10.0154	0.0780	0.91221	−0.00006	0.91215
10.6711	64.2350	.866280	197.7	10.0538	.0771	.91245	−.00010	.91235
21.3112	31.6644	.392277	48.0	9.3726	.0191	.91102	+.00028	.91130
22.1309	28.5029	.390666	47.9	9.6176	.0187	.91099	+.00018	.91117
31.9221	34.2740	.282280	22.6	8.8573	.0092	.91043	+.00009	.91052
42.3567	29.2464	.205021	13.6	9.7692	.0063	.90941	+.00012	.90953

Extrapolated value 0.91310
σ ..... ±0.00008

1.00 atm

11.1544	60.3069	0.866978	277.7	10.4979	0.1222	0.91060	−0.00029	0.91031
22.3219	26.4190	.390304	69.8	9.6914	.0307	.90991	−.00022	.90969
23.9647	23.1569	.306651	66.7	9.9364	.0294	.91004	−.00035	.90969
30.5600	25.0064	.280344	37.8	9.4027	.0166	.90930	−.00007	.90923
31.6170	26.8903	.279376	35.5	9.6969	.0156	.90926	−.00020	.90906
38.3122	25.9995	.230204	24.5	9.2771	.0107	.90837	+.00030	.90867
38.3154	34.8019	.220087	24.5	9.2725	.0108	.90836	+.00030	.90866
40.0074	29.6816	.219191	22.4	9.6362	.0099	.90891	−.00017	.90874

Extrapolated value 0.91102
σ ..... ±0.00009

0.50 atm

17.6963	33.4157	0.523971	232.3	10.0869	0.1171	0.90880	−0.00006	0.90874
17.9560	72.7266	.524275	227.0	10.1915	.1144	.90931	−.00012	.90919
23.6932	24.4505	.401379	125.3	10.3876	.0631	.90925	−.00022	.90903
31.5103	21.4565	.279806	71.4	9.6812	.0360	.90734	+.00011	.90745
44.7281	19.6214	.219747	35.3	10.8154	.0183	.90725	−.00037	.90688
44.8320	29.6347	.219444	36.1	10.8265	.0182	.90718	−.00037	.90681

Extrapolated value 0.90948
σ ..... ±0.00019

	Temperature, °C			
	−30.00	0.00	+50.00	+90.00
	(a) Oxygen			
C_p/R, 1.00 atm	3.5223	3.5264	3.5549	......
$(C_p − 1 − C_p^o)/R$	0.0100	0.0079	0.0055	......
C_p^o/R, observed	3.5123	3.5185	3.5494	......
C_p^o/R, spectroscopic	⁎ 3.5112	3.5207	3.5499	......
Percentage difference, observed-spectroscopic	+0.03	−0.06	−0.01	......
	(b) Carbon dioxide			
C_p/R, 1.50 atm	4.2739	4.4028	4.6463	4.8332
1.00 atm	4.3306	4.3752	4.6324	4.8222
0.50 atm	4.1902	4.3509	4.6184	4.8141
C_p^o/R, observed	4.148	4.324	4.604	4.804
C_p^o/R, spectroscopic:				
Benedict [24]	4.148	4.325	4.600	4.800
Wagman [25]	......	......	4.600	4.799
Percentage difference, observed-spectroscopic	0.00	−0.02	+0.09	+0.08
$\Delta(C_p/R)/\Delta p$, atm⁻¹	.0637	.0519	.0279	.0192

⁎ Corrected for presence of 0.2% of nitrogen.

of C_p/R at 1 atm obtained by those authors were 0.13, 0.04, and 0.08 percent higher than values obtained by interpolation in the present experimental results, at the three temperatures of their experiments: 26.9°, 58.7°, and 94.56° C.

The results at each temperature were extrapolated linearly to zero pressure to obtain the values of (C_p^o/R, observed) listed in table 3 (b). These values were first compared with the most recently published theoretical ones [8, 23] and found to be 0.2 to 0.3 percent higher. Recalculation of the theoretical values was made by W. S. Benedict and independently checked by H. W. Woolley [24]. The results are shown in table 2 on the line labeled "Benedict". Two values interpolated in the National Bureau of Standards tables of "Selected values of chemical thermodynamic properties" [25], which were recalculated by Wagman from the older calculations of Kassel [9], are also given.

A consideration of the possible errors of the various measurements involved in these heat-capacity determinations, as well as the precision of the results, and the agreement of the observed and calculated heat capacities of oxygen, leads to the conclusion that the error in the final values of C_p/R at each pressure should not exceed 0.1 percent. The extrapolated values of C_p^o/R should therefore be reliable to 0.15 percent.

5.3. Equation of State of Carbon Dioxide

It is assumed here that in the low-pressure region covered by these experiments the equation of state of carbon dioxide is of the form

$$pV = RT + Bp, \qquad (2)$$

where B is a function of the temperature. The thermodynamic relation

$$\left(\frac{\partial \frac{C_p}{R}}{\partial p}\right)_T = -\frac{T}{R}\left(\frac{\partial^2 V}{\partial T^2}\right)_p = -\frac{T}{R}\left(\frac{\partial^2 B}{\partial T^2}\right)_p \qquad (3)$$

must be satisfied by the second derivative of the second virial coefficient, B. The values of the change in heat capacity with pressure, obtained in this research, are given in the last line of table 3 and plotted as circles in figure 5. Also in figure 5 are shown curves representing the right-hand side of eq 3 obtained from (1) the recent pVT isotherms of MacCormack and Schneider [13]; (2) the Berthelot equation, using the critical constants of Meyers and Van Dusen [26]; and (3) the Lennard-Jones potential function [27, 28]. The dashed curve affords a comparison with other experimental work through the equation

$$\left(\frac{\partial \frac{C_p}{R}}{\partial p}\right)_T = -\mu\left(\frac{\partial \frac{C_p}{R}}{\partial T}\right)_p - \frac{C_p}{R}\left(\frac{\partial \mu}{\partial T}\right)_p, \qquad (4)$$

where the values of the Joule-Thomson coefficient μ, and its derivative were obtained by interpolation in the tables of Roebuck, Murrell, and Miller [29].

A simple calculation shows that the quantity given by eq 3 is approximately 1 percent of the heat capacity and also 1 percent of the values of the second virial coefficient, in the region covered by this investigation. Therefore, if second virial coefficients could be determined to the same percentage accuracy as the heat capacities, the values of $\partial(C_p/R)/\partial p$ calculated from the right-hand side of eq 3 would be about half as accurate (because of two differentiations) as those obtained from direct heat-capacity
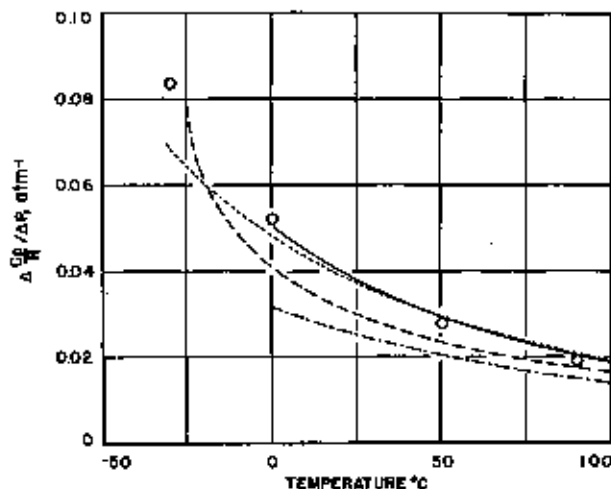

FIGURE 5. *Change of heat capacity of carbon dioxide with pressure as a function of temperature.*

○, This research; ———, MacCormack and Schneider [13]; — — —, Joule-Thomson-Roebuck, Murrell and Miller [19]; ------, Berthelot; ——, Lennard-Jones 6-12 potential function.

measurements. However, the limit of error generally to be expected from good pVT measurements, and that given by MacCormack and Schneider for their work [7], is about 0.5 percent of the value of B in this region. As the heat-capacity measurements are thought to be good to 0.1 percent, the values of $\partial(C_p/R)/\partial p$ obtained in this research are about an order of magnitude more accurate than those calculated from second virial coefficients.

The comparisons made in figure 5 show that the Lennard-Jones function cannot be used successfully to calculate the equation of state of carbon dioxide. An attempt was made to fit new Lennard-Jones constants to the results of this research, but unreasonable values ($b_0 = 25$ cm^3 mole^{-1} and $\epsilon/k = 550°$K) were obtained. The difficulties presented by ellipsoidal molecules such as carbon dioxide have been mentioned by others [28].

The data of state of MacCormack and Schneider are evidently adequate to give good second derivatives of the second virial, as shown by figure 5. Other empirical equations, such as van der Waals' and the Beattie-Bridgeman equation, give curves similar to the Berthelot equation.

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