Thermal Properties of Carbon Dioxide in the Critical Region

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ENTHALPY, ENTROPY, and specific heat of carbon dioxide have been well established for most regions of temperature and pressure (*2, 4, 6, 8*). These tabulations are based largely on the excellent *P-V-T* work of Michels and Michels (*7*). Wentorf (*9*) has made *P-V-T* determinations in the critical region. However, his data cover only the range between 31.02° and 31.10° C. and 72.723 and 72.974 atm. Ellenwood and others (*3*) have calculated the specific heat from the Beattie-Bridgeman equation of state and zero pressure spectroscopic data at intervals of 1000 p.s.i.a. The existing data have been summarized in a recent survey article (*5*). Calculated thermal properties are not reliable in the critical region. This is due to difficulties in computing accurate results from *P-V-T* data. The volume changes so rapidly with pressure and temperature near the critical point, that interpolation is inaccurate. Also the computations involve first, and sometimes second, derivatives of volume and this introduces inaccuracies in numerical work.

Direct experimental determination of the enthalpy as a function of temperature and pressure eliminates most of these difficulties. The entropy along an isobar is obtainable from the enthalpy measurements by the expression:

$$(S_2 - S_1)_p = \left[\int_{H_1}^{H_2} \frac{dH}{T} \right]_p \tag{1}$$

The specific heat can be determined by a single differentiation of the enthalpy results according to the equation:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{2}$$

In the present investigation a flow calorimeter was operated so as to obtain enthalpy *vs.* temperature isobars. This was accomplished by measuring the flow rate, fluid temperatures in and out of the test section (calorimeter), and the electrical energy supplied. The first law of thermodynamics for a steady-state flow process may be written:

$$\Delta H + \frac{\Delta u^2}{2g_c} + \frac{g}{g_c} \Delta z = Q - W_s \tag{3}$$

Since the velocities are small and the calorimeter is horizontal, this expression reduces to

$$Q = \Delta H \tag{4}$$

Assuming that the measured electrical energy is transferred entirely to the flowing fluid, the electrical heat input may be equated to the enthalpy change of the fluid.

APPARATUS AND EXPERIMENTAL PROCEDURE

Figure 1 is a schematic diagram of the apparatus, which is similar to the heat transfer equipment described by Bringer and Smith (*1*). Carbon dioxide (Liquid Carbonic Corp. welding grade, 99.9% purity; major impurity air, 0.05% maximum) is circulated by the canned rotor, centrifugal pump to be heated in the test section and cooled in the aftercooler. Details of the test section, an Inconel tube ¼-inch outside diameter, 22 Birmingham wire gage, and 18 inches long, are shown in Figure 2.

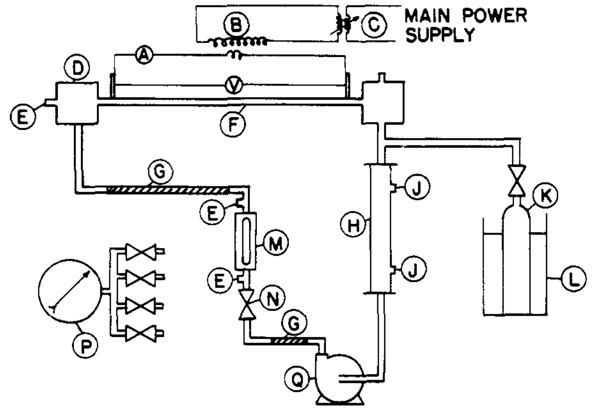

Figure 1. Experimental apparatus

A.	Ammeter	J.	Water inlet or outlet
B.	Transformer	K.	Carbon dioxide cylinder
C.	Variac	L.	Water bath
D.	Mixing chamber	M.	Rotameter
E.	Pressure tap	N.	Flow control valve
F.	Test section	P.	Pressure gage and manifold
G.	Preheater	Q.	Pump
H.	Aftercooler	V.	Voltmeter

The heating was electrical, with the Inconel tube serving as a resistance heater. The energy input was measured with an ammeter and a voltmeter. Flow rates were measured with a rotameter, and fluid temperatures were determined using copper-constantan thermocouples directly immersed in the mixing chamber. The thermocouples were calibrated using the fixed point method. The points chosen were ice, boiling water, and boiling naphthalene. The thermocouples were then inserted in the position shown in Figure 2. The mixing chambers are designed to promote good mixing without causing high pressure drops. At the entrance, the fluid expands into the mixing chamber, and its temperature is measured just before it enters the test section. At the exit, the fluid again expands into the mixing chamber, and its temperature is measured just before it leaves the mixing chamber. Both thermocouples were wrapped with aluminum foil to shield against radiation effects. The pressure was observed with a Heise Bourdon

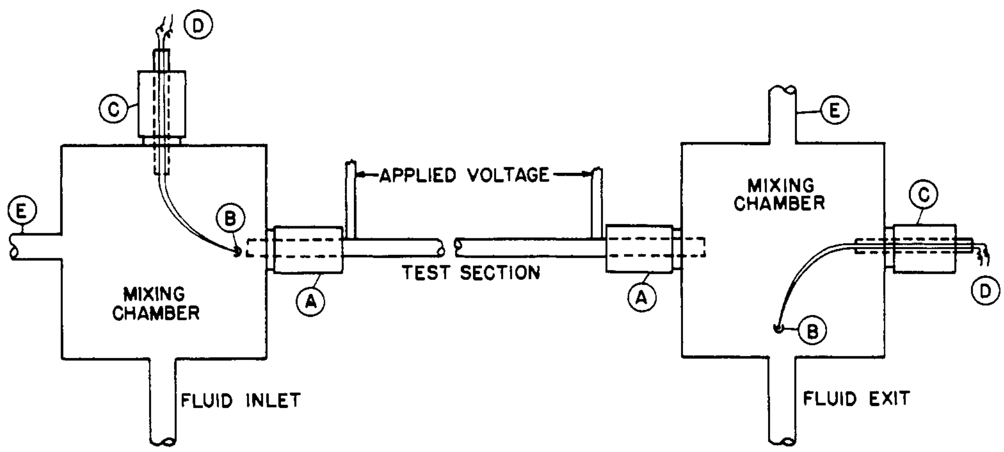

Figure 2. Test section fitting

- *A.* Electrically insulating, pressure-sealing fitting
- *B.* Thermocouple, with radiation shield
- *C.* Pressure-sealing fitting
- *D.* Thermocouple wires, to potentiometer
- *E.* Pressure tap

tube gage, calibrated from 0 to 1500 p.s.i. in 1-p.s.i. increments. The system pressure was maintained by directly connecting a full cylinder of carbon dioxide to the apparatus (Figure 1). The cylinder, filled with liquid, was inserted in a constant-temperature water bath. The Heise gage calibration was checked with a dead weight gage. The test section and mixing chambers were insulated with asbestos tape, Styrofoam, and glass fiber.

The method of operation was to set the flow rate, pressure, and inlet fluid temperature and vary the heat input, noting the corresponding change in the outlet fluid temperature. Data were obtained at pressures of 1050, 1071, 1100, 1125, 1150, and 1200 p.s.i.a. The inlet temperature was held at 65° F.; readings were taken at different outlet temperatures up to 120° F. The thermal properties have been well established outside of this range of temperatures and pressures and are tabulated—for example, by Huggill and others (*4*).

PRECISION OF DATA

The equipment was tested at pressures between 800 and 900 p.s.i.a where the enthalpy is well known. Experimental enthalpy changes agreed well with tabulated values, the maximum observed deviation being 1.0 B.t.u. per pound and the average deviation 0.6 B.t.u. per pound. In the critical region, enthalpy changes between 65° and 120° F. at each pressure were compared with Huggill and others (*4*), and the results of this comparison are shown in Table I. The systematic change of discrepancy with pressure may be due to interpolation error.

Table I. Comparison of Enthalpy Values

P, P.S.I.A.	ΔH, 65 to 120° F. Exptl.	ΔH, 65 to 120° F. Calcd. (*4*)	Deviation, B.t.u./Lb.
1050	90.5	89.3	+1.2
1071	89.4	88.5	+0.9
1100	87.6	87.2	+0.4
1125	86.5	86.1	+0.4
1150	85.0	84.9	+0.1
1200	80.9	82.0	−1.1

Further evidence supporting the absolute accuracy of the investigation is given by the fact that, at 1071 p.s.i.a. (the critical pressure), the steepest ascent of the enthalpy isobar was observed to occur at 87.8° F., the critical temperature. For other pressures, the temperatures at which this phenomenon was observed—i.e., the temperatures of maximum C_p—are given below as transposed critical temperatures.

P, P.S.I.A.	*T*, ° F.	*P*, P.S.I.A.	*T*, ° F.
1100	89.6	1150	93.4
1125	91.4	1200	96.9

The apparatus has been used subsequently in heat transfer studies. These results gave enthalpy changes for the fluid which agreed within 1.0 B.t.u. per pound with the measured electrical energy input in the heat transfer tests. This suggests that the enthalpy values are reproducible.

A flow calorimeter cannot be operated at exactly constant pressure. For this investigation, the flow rate was adjusted to a value low enough to limit pressure drops across the test section to 1.0 p.s.i. The error due to this small change in pressure is negligible except near the critical point, where the error can be as high as 1.0 B.t.u. per pound. As a further check on the error from this source, runs were made at different flow rates. At no time could a change in enthalpy be observed as a result of this change in pressure.

The thermocouples were calibrated to 0.1° C., the limit of accuracy for copper-constantan thermocouples. (Results are reported to 0.1° F. so that engineering units could be used consistently.) The ammeter and voltmeter are accurate to 0.5% of full scale and were always operated above half scale. As a further check on these readings the resistance of the test section was measured to 0.3% on a Wheatstone bridge. The rotameter was calibrated to 1.0% of full scale by the manufacturer. Further calibration showed that this level of accuracy could be maintained over most of the rotameter range by using only discrete values of the flow rate as located by marks on the tube.

RESULTS

The experimental data consisted of enthalpy values above 65° F. for the several pressures studied. To be consistent with earlier tabulations of data (*8*), it was desirable to report the results on the basis of H and $S = 0$ for saturated liquid at −40° F. This requires a knowledge of the enthalpy change between the reference state at −40° F. and 65° F. for each pressure. Since 65° F. is relatively far removed from the critical temperature, calculated values (*4*) are reliable for this adaptation. Plotting and smoothing the experimental data, corrected to the reference state, resulted in the *P-H* diagram given in Figure 3. The saturation envelope and single-phase values at pressures below 1050 p.s.i.a were taken directly from Huggill's results (*4*).

To obtain entropy data, smooth plots of H *vs.* $1/T$ at each pressure were prepared from the enthalpy curves. Integration under these plots gave entropy *vs.* temperature information, as shown by Equation 1. Figure 4 is the final *T-S* diagram. Again, the saturation envelope, and 60-, 65-, 90-, 100-, and 150-atm. isobars shown in Figure 4 were taken from Huggill and others.

Figure 5 is a plot of C_p *vs.* temperature obtained by differentiation of the enthalpy data as required by Equation 4. This was accomplished by taking differences of successive data points, plotting a bar graph of $\Delta H/\Delta t$ *vs.* t, and drawing an equal area under the bars. The dotted portions of the lines represent extrapolation of values into the region where the derivatives are too high to be determined accurately. Ellenwood and others (*3*) have calculated the specific heat at high pressures. In the critical region, they present values at 1000 and 2000 p.s.i.a. Comparison of their value at 1000 p.s.i.a. and 120° F. with the value estimated from Figure 5 gave good agrrement.

Numerical values of the thermal properties are presented in Table II at small intervals of temperature and pressure. The enthalpy values have been smoothed to give consistent differences. The maximum correction used for smoothing was 0.2 B.t.u. per pound, which is well within the experimental accuracy of the data. Before smoothing, the

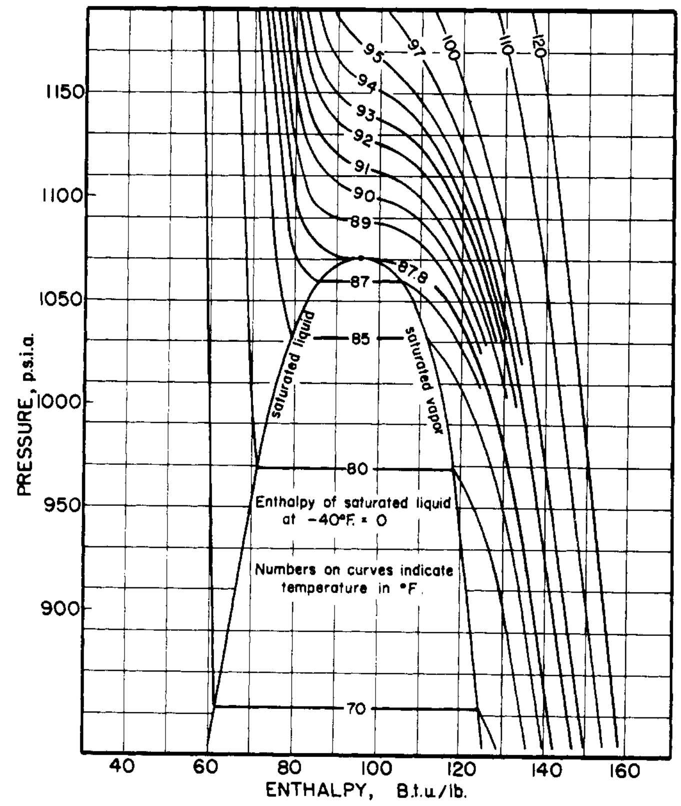

Figure 3. Pressure-enthalpy diagram

Values below 1050 p.s.i.a taken from Huggill and others (*3*)

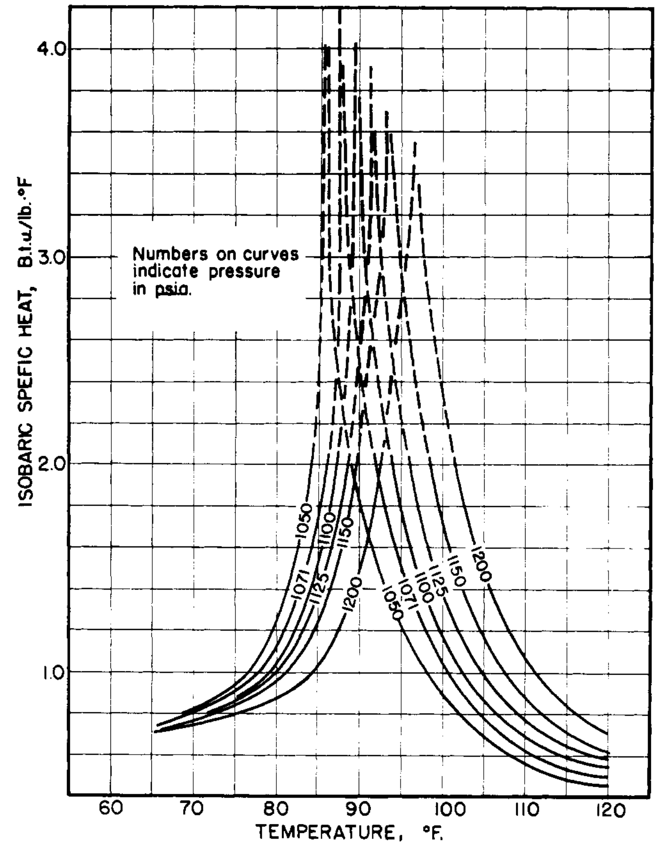

Figure 5. Isobaric specific heat

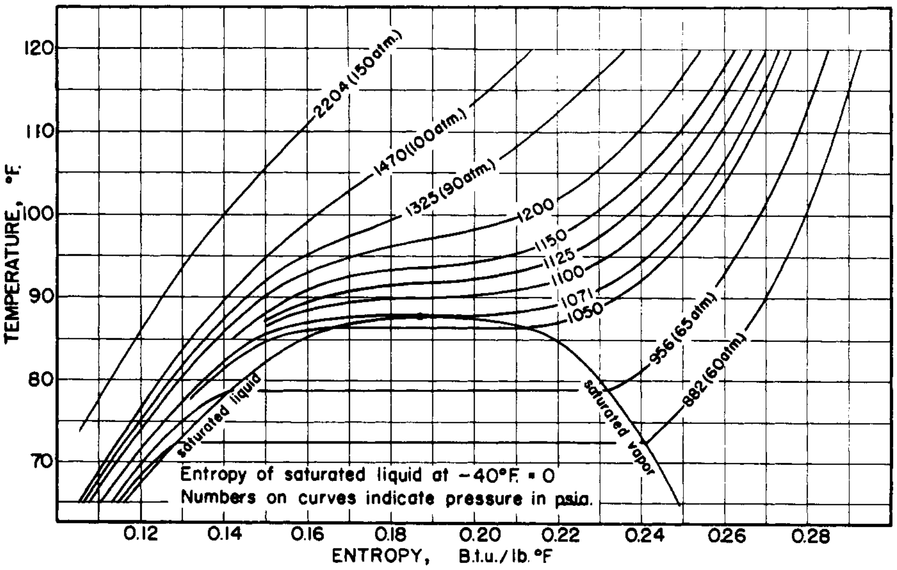

Figure 4. Temperature-entropy diagram

Isobars above 60 atm. from Huggill and others (*3*)

Table II. Thermal Properties of Carbon Dioxide in the Critical Region[a]

		Temp., ° F.								
P, P.S.I.A.		65	70	80	85	87	87.8	89	90	91
1050	H	55.5	59.2	68.8	76.9	112.2	115.4	118.7	121.2	123.2
	S	0.1111	0.1178	0.1360	0.1521	0.2186	0.2245	0.2301	0.2338	0.2369
	C_p	0.74	0.83	1.26	2.38	...	...	...	...	...
1071	H	55.3	58.8	68.3	75.0	79.8	95.8	113.6	117.2	119.5
	S	0.1106	0.1173	0.1350	0.1479	0.1556	0.1862	0.2188	0.2251	0.2298
	C_p	0.74	0.82	1.15	1.80	...	∞	...	...	...
1100	H	55.0	58.6	67.8	74.1	77.8	80.0	83.8	98.5	109.5
	S	0.1100	0.1166	0.1339	0.1450	0.1520	0.1552	0.1629	0.1850	0.2105
	C_p	0.73	0.81	1.05	1.55	1.99	...	...	...	...
1125	H	54.8	58.3	67.2	73.1	76.2	77.7	80.2	83.1	87.5
	S	0.1094	0.1160	0.1328	0.1433	0.1491	0.1517	0.1567	0.1630	0.1738
	C_p	0.73	0.79	1.01	1.40	1.68	1.84	...	...	...
1150	H	54.6	58.1	66.7	72.2	74.9	76.1	78.1	79.9	82.2
	S	0.1088	0.1154	0.1318	0.1417	0.1464	0.1487	0.1522	0.1559	0.1601
	C_p	0.72	0.78	0.96	1.27	1.47	1.60	1.84	2.16	...
1200	H	54.2	57.6	65.7	70.2	72.5	73.5	75.1	76.6	78.2
	S	0.1078	0.1143	0.1298	0.1387	0.1427	0.1444	0.1471	0.1497	0.1521
	C_p	0.71	0.75	0.87	1.05	1.17	1.25	1.37	1.51	1.76

		Temp., ° F.							
		92	93	94	95	97	100	110	120
1050	H	124.8	126.3	127.6	128.9	131.0	133.9	141.0	146.0
	S	0.2398	0.2421	0.2441	0.2461	0.2499	0.2547	0.2669	0.2761
	C_p	...	1.43	1.32	1.24	1.08	0.90	0.56	0.46
1071	H	121.4	123.2	124.9	126.2	128.4	131.3	139.2	144.7
	S	0.2331	0.2360	0.2387	0.2411	0.2451	0.2505	0.2637	0.2728
	C_p	...	...	1.58	1.37	1.26	1.02	0.62	0.50
1100	H	114.6	117.3	119.4	121.3	124.4	128.0	136.9	142.6
	S	0.2202	0.2255	0.2289	0.2319	0.2371	0.2437	0.2585	0.2694
	C_p	...	...	...	1.80	1.48	1.18	0.70	0.55
1125	H	100.7	109.7	112.9	115.9	119.8	124.3	134.7	141.3
	S	0.1950	0.2071	0.2151	0.2208	0.2282	0.2365	0.2539	0.2662
	C_p	...	...	...	...	1.82	1.40	0.78	0.58
1150	H	85.1	89.7	101.1	108.1	114.3	120.7	132.4	139.6
	S	0.1652	0.1752	0.1957	0.2072	0.2180	0.2285	0.2491	0.2626
	C_p	...	...	...	...	2.51	1.78	0.89	0.62
1200	H	79.8	81.7	84.2	86.8	97.1	111.0	126.6	135.1
	S	0.1552	0.1591	0.1641	0.1698	0.1875	0.2116	0.2387	0.2542
	C_p	1.88	2.15	...	...	...	...	1.11	0.70

[a] Reference state: H and $S = 0$ for saturated liquid at −40° F.; H in B.t.u./lb.; S and C_p in B.t.u./lb. ° R.

maximum deviation of the data from smooth curves was 0.3 B.t.u. per pound.

The data presented here serve to define the general behavior of thermal properties in the near-critical region. The results are subject to some errors as discussed, but are more accurate than any previously available.

ACKNOWLEDGMENT

The financial assistance of the Office of Ordnance Research, Contract, DA-11-022-ORD-2674, which made this work possible, is gratefully acknowledged.

NOMENCLATURE

C_p = isobaric specific heat, B.t.u per pound ° R.
g = acceleration of gravity, ft./sec.^{2}
g_c = gravitational conversion constant, 32.17 ft. lb.$_m$/sec.^{2} lb.$_f$
H = enthalpy, B.t.u./lb.
P = pressure, p.s.i.
Q = heat transfer rate, B.t.u./lb. of flowing fluid
S = entropy, B.t.u./lb. ° R.
t = temperature, ° F.
T = temperature, ° R.
u = velocity, ft./sec.
v = volume, cu. ft./lb.
W_s = shaft work, B.t.u./lb. of flowing fluid
z = elevation, ft.

Subscripts

p = constant pressure
T = constant temperature

LITERATURE CITED

(1) Bringer, R.P., Smith, J.M., *A.I.Ch.E. Journal* **3**, 49 (1957).
(2) Cramer, F., *Chem. Ing. Tech.* **27**, 484 (1955).
(3) Ellenwood, F.O., Kulik, Nickolas, Gay, W.R., Cornell Univ., Eng. Exptl. Sta. Bull. **30** (1942).
(4) Huggill, J.A., Newitt, D.M., Pai, M.U., Kuloor, N.R., in "Thermodynamic Functions of Gases," Din, F., ed., vol. **1**, Butterworths, London, 1956.
(5) Liley, P.E., J. CHEM. ENG. DATA **4**, 238 (1959).
(6) Michels, A., de Groot, S.R., *Appl. Sci. Research* **A1**, 94 (1948).
(7) Michels, A., Michels, C., *Proc. Roy. Soc. (London)* **A153**, 201 (1953).
(8) Plank, R., Kuprianoff, J., *Z. ges. Kalte-Ind.* **36**, 41 (1929).
(9) Wentorf, R.H., *J. Chem. Phys.* **24**, 607 (1956).

RECEIVED for review March 31, 1960. Accepted July 1, 1960.