system 11 is not significant. Of the remaining sixteen systems, which should all follow the new rule, seven (1-5, 7, and 16, all containing hydrocarbons of $CHCl_3$) follow the geometric mean rule, three (19-21, all containing a hydrocarbon plus a fluorocarbon) follow an empirical modification of the new rules, and only six (6, 10, 12, 13, 14, and 18) follow the new rules strictly.

The best calculated values for B_{12} are quite close to the experimental values. The mean of the absolute per cent deviation of the calculated value from experimental value is 9.7%.

Since the absolute per cent deviation in the calculated values for B_{12} and for B_{11} and B_{22} are all approximately 10, the maximum mean deviation in B_m for a binary mixture calculated in the ways described will be 10%:

$$B_m = B_{11}x_1^2 + 2B_{12}x_1x_2 + B_{22}x_2^2$$

$$\delta B_m = x_1^2\delta B_{11} + 2x_1x_2\delta B_{12} + x_2^2\delta B_{22}$$

$$\delta B_{11}/B_{11} = \delta B_{22}/B_{22} = \delta B_{12}/B_{12} = \Delta = 10\%$$

$$\delta B_m = (x_1^2B_{11} + 2x_1x_2B_{12} + x_2^2B_{22})\Delta$$

$$\delta B_m = B_m\Delta$$

$$\delta B_m/B_m = \Delta = 10\%$$

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Equation of State Prediction of Thermodynamic Properties of Carbon Dioxide

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A table and graph of the thermodynamic properties for CO_2 are presented for the critical ragion. Graphs are given for the effect of pressure on enthalpy for CO_2 for reduced temperature of 1.1 and 1.4 and for reduced pressures up to 6.0. All values are calculated from an equation of state and a low-pressure heat capacity equation. Comparisons are made with experimental data where available.

THE TWO objectives of this work are: to show how an accurate equation of state can safely predict changes in thermodynamic properties, and to present a completely consistent set of thermodynamic properties for CO_2 in the critical region. Fortunately, there are some experimental data available to which the predictions of the equation of state may be compared.

CALCULATION OF THE THERMODYNAMIC PROPERTIES

Few compounds have been studied more extensively than CO_2. There have been many investigations of the *P-V-T* and thermal behavior. A recent investigation by Koppel and Smith (*1*) is of particular importance because it includes thermal data for the region around the critical point. This region also was the object of considerable study in the development of an equation of state (*3*, *4*) to represent the *P-V-T* behavior. The equation which was designed specifically to have the correct curvature in the neighborhood of the critical point is

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2\exp(-kT)}{(V-b)^2} + \frac{A_3 + B_3T + C_3\exp(-kT)}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{A_5 + B_5T + C_5\exp(-kT)}{(V-b)^5} \quad (1)$$

where for P in p.s.i.a., T in °R., and V in lb./ft.^{3}, the constants are for CO_2.

Table I. Thermodynamic Properties of CO_2 in the Critical Region

Temp., °F.	Property[a]	Pressure, p.s.i.a.								
		1050		1069.4		1071		1100		1125
		K. & S(1)	Calcd.	K. & S.[b]	Calcd.	K. & S.	Calcd.	K. & S.	Calcd.	K. & S.
65	V		0.01985	...	0.01981		0.01981		0.01976	
	H	55.5	57.3	...	57.2	55.3	57.2	55.0	57.0	54.8
	S	0.1111	0.1145	...	0.1141	0.1106	0.1141	0.1100	0.1135	0.1094
70	V		0.02046	...	0.02041		0.02041		0.02034	
	H	59.2	61.9	...	61.7	58.8	61.7	58.6	61.5	58.3
	S	0.1178	0.1233	...	0.1228	0.1173	0.1227	0.1166	0.1221	0.1160
80	V		0.02222	...	0.02208		0.02206		0.02188	
	H	68.8	71.3	...	70.9	68.3	70.8	67.8	70.3	67.2
	S	0.1360	0.1407	...	0.1398	0.1350	0.1398	0.1339	0.1386	0.1328
85	V		0.02434	...	0.02380		0.02376		0.02325	
	H	76.9	78.3	...	77.0	75.0	76.9	74.1	75.7	73.1
	S	0.1521	0.1536	...	0.1512	0.1479	0.1510	0.1450	0.1485	0.1433
87	V		0.04958	...	0.02568		0.02555		0.02425	
	H	112.2	113.9	...	81.9	79.8	81.6	77.8	78.8	76.2
	S	0.2186	0.2188	...	0.1600	0.1556	0.1595	0.1520	0.1541	0.1491
87.8	V		0.05266	...	0.03454[c]		0.02892[d]		0.02489	
	H	115.4	116.8	...	100.7	95.8	88.2	80.0	80.4	77.7
	S	0.2245	0.2242	...	0.1944	0.1862	0.1716	0.1552	0.1572	0.1517
89	V		0.05590	...	0.04910		0.04838		0.02675	
	H	118.7	119.8	...	114.1	113.6	113.4	83.8	84.7	80.2
	S	0.2301	0.2296	...	0.2189	0.2188	0.2177	0.1629	0.1649	0.1567
90	V		0.05803	...	0.05241		0.05187		0.03487	
	H	121.2	121.7	...	117.3	117.2	116.9	98.5	98.2	83.1
	S	0.2338	0.2331	...	0.2248	0.2251	0.2239	0.1850	0.1896	0.1630
91	V		0.05985	...	0.05488		0.05443		0.04393	
	H	123.2	123.3	...	119.6	119.5	119.3	109.5	109.7	87.5
	S	0.2369	0.2360	...	0.2290	0.2298	0.2283	0.2105	0.2104	0.1738
92	V		0.06148	...	0.05692		0.05652		0.04809	
	H	124.8	124.7	...	121.5	121.4	121.2	114.6	114.2	100.7
	S	0.2398	0.2385	...	0.2324	0.2331	0.2319	0.2202	0.2186	0.1950
93	V		0.06296	...	0.05870		0.05833		0.05097	
	H	126.3	126.0	...	123.1	123.2	122.9	117.3	117.1	109.7
	S	0.2421	0.2408	...	0.2353	0.2360	0.2348	0.2255	0.2239	0.2071
94	V		0.06433	...	0.06029		0.05994		0.05325	
	H	127.6	127.1	...	124.5	124.9	124.3	119.4	119.3	112.9
	S	0.2441	0.2429	...	0.2379	0.2387	0.2374	0.2289	0.2279	0.2151
95	V		0.06561	...	0.06174		0.06141		0.05518	
	H	128.9	128.2	...	125.9	126.2	125.6	121.3	121.2	115.9
	S	0.2461	0.2449	...	0.2402	0.2411	0.2398	0.2319	0.2313	0.2208
97	V		0.06795	...	0.06433		0.06403		0.05842	
	H	131.0	130.1	...	128.1	128.4	127.9	124.4	124.2	119.8
	S	0.2499	0.2484	...	0.2442	0.2451	0.2439	0.2371	0.2367	0.2282
100	V		0.07106	...	0.06770		0.06742		0.06235	
	H	133.9	132.7	...	130.0	131.3	130.8	128.0	127.8	124.3
	S	0.2547	0.2530	...	0.2494	0.2505	0.2490	0.2437	0.2431	0.2365
110	V		0.07949	...	0.07653		0.07628		0.07196	
	H	141.0	139.5	...	138.3	139.2	138.2	136.9	136.2	134.7
	S	0.2669	0.2651	...	0.2624	0.2637	0.2621	0.2585	0.2579	0.2539
120	V		0.08630	...	0.08349		0.08326		0.07920	
	H	146.0	145.0	...	144.0	144.7	143.9	142.6	142.3	141.3
	S	0.2761	0.2746	...	0.2723	0.2728	0.2721	0.2694	0.2686	0.2662

[a] *V* = cu. ft./lb.; *H* = B.t.u./lb.; *S* = B.t.u./lb.-° R., based on reference state of saturated liquid at −40° F. [b] Not determined by Koppel and Smith (*1*) at this pressure. [c] Critical point used in the development of the equation of state. [d] Critical point taken by Koppel and Smith (*1*).

Pressure, P.s.i.a.				
1125	1150		1200	
Calcd.	K. & S.	Calcd.	K. & S.	Calcd.
0.01972		0.01968		0.01960
56.8	54.6	56.6	54.2	56.3
0.1130	0.1088	0.1125	0.1078	0.1114
0.02028		0.02023		0.02013
61.3	58.1	61.1	57.6	60.7
0.1215	0.1154	0.1210	0.1143	0.1199
0.02174		0.02161		0.02140
69.9	66.7	69.6	65.7	69.0
0.1377	0.1318	0.1369	0.1298	0.1353
0.02293		0.02268		0.02229
74.9	72.2	74.3	70.2	73.3
0.1469	0.1417	0.1466	0.1387	0.1434
0.02369		0.02331		0.02276
77.5	74.9	76.6	72.5	75.2
0.1516	0.1464	0.1497	0.1427	0.1469
0.02410		0.02362		0.02298
78.7	76.1	77.6	73.5	76.1
0.1538	0.1487	0.1516	0.1444	0.1484
0.02496		0.02420		0.02335
81.0	78.1	79.4	75.1	77.4
0.1580	0.1522	0.1548	0.1471	0.1508
0.02618		0.02486		0.02372
83.9	79.9	81.2	76.6	78.6
0.1633	0.1559	0.1581	0.1497	0.1531
0.02926		0.02585		0.02416
89.9	82.2	83.6	78.2	80.0
0.1742	0.1601	0.1625	0.1521	0.1555
0.03634		0.02771		0.02471
101.0	85.1	87.5	79.8	81.6
0.1943	0.1652	0.1696	0.1552	0.1584
0.04325		0.03168		0.02545
108.6	89.7	94.6	81.7	83.5
0.2082	0.1752	0.1824	0.1591	0.1619
0.04619		0.03689		0.02654
113.0	101.1	101.6	84.2	86.0
0.2161	0.1957	0.1966	0.1641	0.1664
0.04900		0.04135		0.02829
116.0	108.1	108.2	86.8	89.6
0.2215	0.2072	0.2071	0.1698	0.1730
0.05321		0.04738		0.03415
120.3	114.3	115.2	97.1	99.7
0.2292	0.2180	0.2196	0.1875	0.1911
0.05786		0.05316		0.04280
124.8	120.7	121.2	111.0	111.5
0.2372	0.2285	0.2304	0.2116	0.2123
0.06831		0.06471		0.05764
134.3	132.4	132.3	126.6	127.8
0.2551	0.2491	0.2500	0.2387	0.2411
0.07582		0.07254		0.06626
140.9	139.6	139.4	135.1	136.2
0.2655	0.2626	0.2724	0.2542	0.2557

$R = 0.24381$
$b = 0.007495$
$A_2 = -8.9273631$
$B_2 = 5.262476 \times 10^{-3}$
$C_2 = -150.97587$
$A_3 = 0.17948621$
$B_3 = -5.770542 \times 10^{-5}$
$C_3 = 4.705805$
$A_4 = -2.112459 \times 10^{-3}$
$A_5 = 7.017835 \times 10^{-6}$
$B_5 = 1.023511 \times 10^{-8}$
$C_5 = -4.55437 \times 10^{-4}$
$k = 0.01$

This equation has been shown to represent the P-V-T behavior of CO_2 with good precision up to a density of about 1.5 times the critical.

In addition to the equation of state, an excellent equation for the constant-volume heat capacity at low pressure has been presented (*10*) in the form,

$$C_V = \alpha + \frac{\beta}{T} + \frac{\gamma}{T^2} \qquad (2)$$

where for C_V in B.t.u./lb. mole-° R., and T in ° R.

$\alpha = 14.214$
$\beta = -6.53 \times 10^3$
$\gamma = 1.41 \times 10^6$

As is well-known and fully described (*2*), it is very simple to calculate the changes of enthalpy and entropy in the single phase region by using Equations 1 and 2. The results of these calculations are presented in the table, where they are compared with the experimental values of Koppel and Smith. The comparison is by no means exact, but it is not bad either. This can also be seen in Figure 1, where the enthalpy data of the table have been plotted. The figure shows the ability of the equation of state to predict the correct slopes and trend of enthalpy in a region where the changes are taking place rapidly. In this case Equation 1 is good for all densities up to about 1.5 times the critical density. It begins to deviate appreciably at higher densities. The effect is noticed in the table at temperatures less than 85° F., where the volumes are equal to or less than 0.023

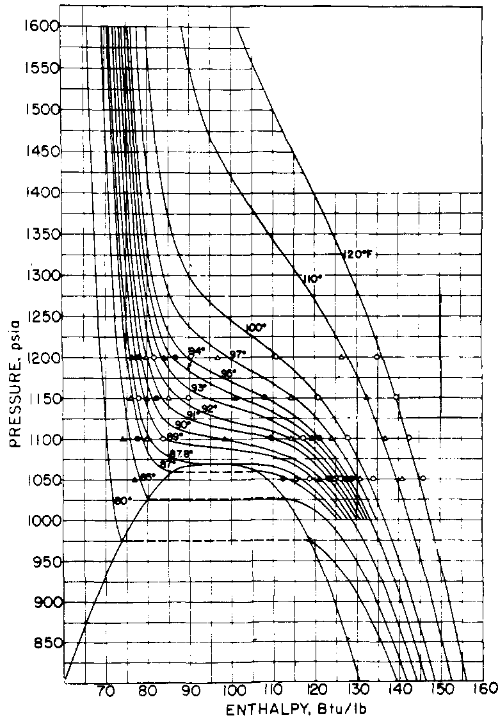

Figure 1. Pressure enthalpy diagram for CO_2

Reference point: H = O for saturated liquid at −40° F. Curves from equation of state. Data points from Koppel and Smith at given temperatures ft.^{3}/lb. which is two-thirds the critical volume. It is readily observed that the calculated enthalpies and entropies check the experimental values much better above 85° F. than below it. This is true everywhere except right at the critical point itself where the possible deviations are extremely large as noted on the critical isotherm.

Also the critical point for the equation of state is not exactly the critical point taken by Koppel and Smith. If their critical point had been used in developing the equation of state, the agreement would have been better in this region. The over-all agreement between the experimental data points and the calculated curves substantiates the equation state.

In view of the success of the equation of state in the critical region, further calculations were made by the same technique at temperatures well above the critical. Obert (*6*) had made comparisons at reduced temperatures of 1.1 and 1.4, and had drawn the conclusion that the Martin-Hou equation (Equation 1) predicted the *P-V-T* behavior nicely at densities below the critical but that perceptible error in enthalpy deviation occurred at a density of only $0.5\rho_c$. This behavior seemed strange because it would certainly not be expected that the equation of state would agree with the enthalpy data in a rather difficult region and fail in a somewhat simpler region even though it represents the *P-V-T* behavior well in both regions. Consequently, new calculations were made here and plotted on Obert's graphs as the open circles in Figures 2 and 3. The source of Obert's experimental data is not known, but recourse was made to the published data (*5, 7, 8, 9*) in the desired ranges and these points were added to the graphs. In both cases it is clear that the open circles, which are the direct consequence of Equations 1 and 2, represent the experimental data within their precision or difference between the several investigators. Evidently, some error must have crept into Obert's calculations to have yielded the M-H line which he presented, for his curve should have followed the open circles.

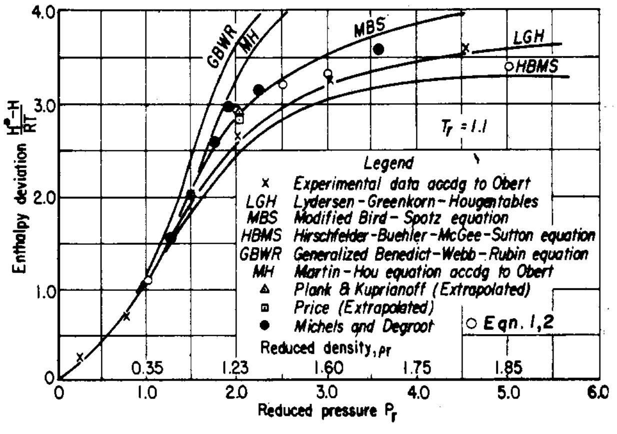

Figure 2. Effect of pressure on enthalpy of CO_2 at a reduced temperature of 1.1

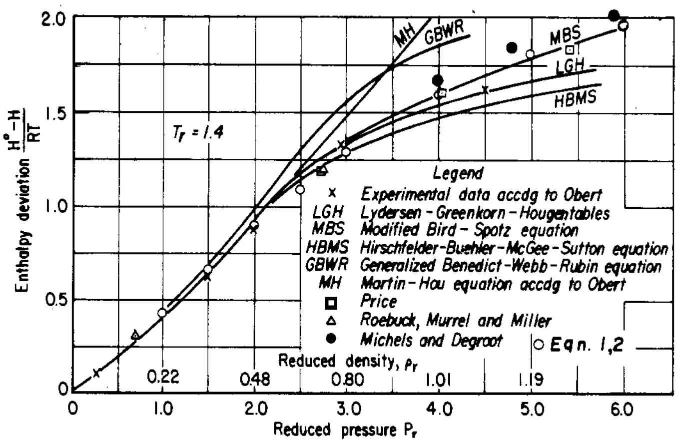

Figure 3. Effect of pressure on enthalpy of CO_2 at a reduced temperature of 1.4

The conclusion to be drawn from this study is that if a relation such as Equation 1 does represent the true *P-V-T* behavior of a substance, then that equation may be safely used to predict changes in enthalpy and entropy in the regions for which the equation is applicable.

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