Thermodynamic Functions of Carbon Dioxide

Joule-Thomson Coefficient, Isochoric Heat Capacity, and Isentropic Behavior at 100° to 1000° C. and 50 to 1400 Bars

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Computation of the thermodynamic functions from pressure-volume-temperature (P-V-T) data for carbon dioxide in the range, 200° to 100° C. and 100 to 1400 bars, has been extended. Previously obtained entropy values have been used to show that the isentropic pressure-volume exponent approximates a linear function of pressure. Previously computed values of PV, its temperature derivative, and the isobaric heat capacity have been used in conjunction with additional computation to obtain values of the Joule-Thomson coefficient and the isochoric heat capacity. These values have been compared with others in the small range of overlap, and maximum error in the computation estimated. As in the previous work, the region of greatest accuracy is believed to be that of simultaneously high temperature and low pressure – e.g., 400° to 100° C. and 50 to 400 bars.

In a previous report (4), P-V-T measurements made by Kennedy (2) on carbon dioxide were used to obtain smoothed values of the product (PV) from which the enthalpy, entropy, and isobaric heat capacity were computed at 100° to 1000° C. and 50 to 1400 bars. These data have been used to compute the internal, kinetic, and free energies (5), and to determine the isentropic behavior of this gas. They have also been used in conjunction with additional computation to obtain values for the Joule-Thomson coefficient and the isochoric heat capacity.

ISENTROPIC BEHAVIOR

The range in temperature of the present data (up to 1000° C.) is of particular interest because it permits determination of isentropes from ambient conditions up to 1400 bars. Other data terminate at too low a temperature to define much of the isentrope above room temperature.

To determine the isentropes, an inverse interpolation of the entropy, S (P,T), and PV (P,T) data previously reported (4), was carried out. A method of divided differences based on a cubic polynomial and equivalent to 4 point Lagrangian interpolation was used.

Tables I and II contain respectively the temperature and PV as functions of entropy and pressure. The entropy intervals have been made small enough for linear interpolation, and the entropy region covered is that expected for ambient conditions.

From these data, it was found that

$$-\left(\frac{\partial \ln P}{\partial \ln V}\right)_S = \alpha \tag{1}$$

approximated a linear function of pressure. The isentropic relationship for carbon dioxide is accordingly approximated by

$$\frac{PV^{\alpha_0}}{1 + bP} = \text{constant, S constant} \tag{2}$$

where α_0 and b are constants.

For the isentrope S = 0.773 (ambient conditions of 25° C. and 760 mm. Hg.), volume in Amagat units and pressure in bars

$$\alpha = 1.244\ (1 + 0.00009825P) \tag{3}$$

TABLE I. TEMPERATURE AS A FUNCTION OF PRESSURE AND ENTROPY FOR CARBON DIOXIDE

Pressure, Bars	Entropy[a], Cal./Mole-Degree 0.573	0.623	0.673	0.723	0.773[h]	0.823	0.873	0.923	0.973
50	359.70	362.38	365.08	367.78	370.50	373.22	375.96	378.70	381.45
100	448.72	451.64	454.56	457.50	460.44	463.40	466.36	469.34	472.32
150	502.73	505.77	508.83	511.89	514.96	518.05	521.14	524.25	527.36
200	542.30	545.44	548.59	551.75	554.92	558.10	561.30	564.50	567.71
250	573.93	577.15	580.38	583.62	586.87	590.14	593.42	596.70	600.00
300	600.46	603.75	607.05	610.36	613.68	617.01	620.36	623.72	627.08
350	623.35	626.69	630.05	633.42	636.80	640.19	643.60	647.01	650.44
400	643.39	646.79	650.20	653.62	657.06	660.50	663.96	667.43	670.91
450	661.30	664.74	668.20	671.67	675.15	678.64	682.15	685.66	689.19
500	677.55	681.04	684.54	688.05	691.57	695.10	698.65	702.21	705.78
600	706.23	709.79	713.36	716.94	720.53	724.15	727.76	731.40	735.04
700	730.86	734.48	738.11	741.75	745.41	749.08	752.75	756.45	760.15
800	752.42	756.09	759.76	763.45	767.15	770.87	774.59	778.33	782.08
900	771.51	775.21	778.92	782.65	786.38	790.13	793.89	797.66	801.44
1000	788.56	792.29	796.02	799.77	803.54	807.31	811.09	814.88	818.69
1100	803.95	807.69	811.44	815.20	818.98	822.76	826.56	830.36	834.18
1200	817.97	821.72	825.49	829.27	833.06	836.87	840.68	844.50	848.34
1300	830.72	834.50	838.29	842.09	845.90	849.72	853.56	857.40	861.25
1400	842.49	846.29	850.10	853.92	857.76	861.60	865.45	869.32	873.19

[a] zero point at 0° C. and 1 atm.
[b] Value at 25° C. and 1 atm.

TABLE II. THE PRODUCT, PV, AS A FUNCTION OF PRESSURE AND ENTHROPY FOR CARBON DIOXIDE

PV (bar - Amagat Unit)

Pressure, Bars	Entropy[a], Cal./Mole-Degree								
	0.573	0.623	0.673	0.723	0.773[b]	0.823	0.873	0.923	0.973
50	2.3515	2.3622	2.3729	2.3837	2.3945	2.4053	2.4162	2.4271	2.4380
100	2.7085	2.7203	2.7322	2.7441	2.7560	2.7680	2.7800	2.7920	2.8041
150	2.9433	2.9558	2.9684	2.9810	2.9936	3.0062	3.0189	3.0316	3.0444
200	3.1293	3.1423	3.1554	3.1684	3.1816	3.1947	3.2079	3.2211	3.2344
250	3.2960	3.3095	3.3230	3.3365	3.3501	3.3637	3.3773	3.3909	3.4046
300	3.4498	3.4636	3.4774	3.4912	3.5050	3.5189	3.5328	3.5468	3.5608
350	3.5940	3.6080	3.6220	3.6360	3.6501	3.6642	3.6783	3.6925	3.7067
400	3.7308	3.7449	3.7590	3.7732	3.7874	3.8017	3.8160	3.8303	3.8447
450	3.8632	3.8775	3.8918	3.9062	3.9206	3.9351	3.9496	3.9641	3.9787
500	3.9887	4.0032	4.0176	4.0322	4.0468	4.0614	4.0760	4.0907	4.1055
600	4.2292	4.2441	4.2590	4.2739	4.2888	4.3038	4.3188	4.3339	4.3490
700	4.4565	4.4716	4.4868	4.5020	4.5172	4.5324	4.5477	4.5630	4.5784
800	4.6714	4.6866	4.7018	4.7171	4.7324	4.7477	4.7631	4.7785	4.7939
900	4.8838	4.8991	4.9145	4.9298	4.9452	4.9606	4.9761	4.9915	5.0070
1000	5.0817	5.0969	5.1121	5.1273	5.1425	5.1578	5.1731	5.1884	5.2038
1100	5.2765	5.2917	5.3069	5.3221	5.3374	5.3526	5.3679	5.3832	5.3986
1200	5.4650	5.4799	5.4949	5.5098	5.5248	5.5398	5.5549	5.5699	5.5850
1300	5.6455	5.6603	5.6751	5.6899	5.7047	5.7196	5.7345	5.7494	5.7644
1400	5.8292	5.8441	5.8590	5.8740	5.8890	5.9040	5.9190	5.9341	5.9491

[a] Zero point at 0° C. and 1 atm.
[b] Value at 25° C. and 1 atm.

and the expression

$$PV^{\alpha_0}/(1 + bP) \qquad (4)$$

is constant to ±0.1% for 0 to 200 bars. Moreover, for other isentropes in Table II, the constants of Equation 3 can be used to evaluate Expression 4 at the 100-bar value of PV. If this is done, Equation 2 predicts the volume within 0.2% in the region of 50 to 200 bars.

Although α is a monotonically increasing function of P over the range 50 to 1400 bars, the linear approximation is not nearly as good above 200 bars. It is much better, however, than the frequently used approximation that α is a constant.

The P-T isentropic exponent shows a behavior analagous to that of α. A more detailed description of the isentropic behavior is given by Price and Lalos (7).

COMPUTATIONS

The Joule-Thomson coefficient, μ, was computed from the relationship

$$\mu = \frac{1}{PC_P}\left\{T\left[\frac{\partial(PV)}{\partial T}\right]_P - PV\right\} \qquad (5)$$

TABLE III. JOULE-THOMSON COEFFICIENT FOR CARBON DIOXIDE AS A FUNCTION OF TEMPERATURE AND PRESSURE

μ (degree/bar) x 10^2

Pressure, Bars	Temperature, ° C.													
	100	150	200	250	300	350	400	450	500	600	700	800	900	1000
50	61.2	46.0	35.0	26.9	21.0	16.4	12.9	10.4	8.67	6.26	4.44	3.20	2.43	2.03
100	55.0	41.0	30.7	24.0	19.0	14.9	11.9	9.82	8.17	5.58	3.55	2.18	1.24	0.43
150	40.0	33.7	26.7	21.9	17.9	14.4	11.3	8.98	7.26	4.88	3.13	1.92	0.97	0.12
200	25.2	26.1	23.0	18.9	15.3	12.2	9.40	7.58	6.18	4.20	2.65	1.54	0.65	-0.08
250	15.2	19.1	18.9	16.7	13.7	10.9	8.58	6.68	5.37	3.59	2.33	1.23	0.37	-0.47
300	9.61	13.9	15.6	13.8	11.7	9.54	7.72	6.05	4.75	3.01	1.75	0.80	-0.14	-0.88
350	6.45	10.0	11.7	11.8	10.1	8.15	6.54	5.06	3.82	2.14	1.02	0.15	-0.62	-1.29
400	4.35	7.27	8.91	9.52	8.83	6.84	5.47	4.20	3.08	1.49	0.47	-0.32	-1.04	-1.60
450	2.98	5.25	6.61	7.62	7.29	5.97	4.89	3.98	2.94	1.07	-0.04	-0.80	-1.42	-1.90
500	1.94	3.79	5.10	6.18	5.98	5.11	4.36	3.65	2.70	0.91	-0.30	-1.10	-1.77	-2.29
600	0.47	1.91	2.77	3.40	3.57	3.45	3.12	2.55	1.81	0.36	-0.80	-1.56	-2.32	-3.15
700	-0.35	0.60	1.19	1.58	1.76	1.89	1.96	1.67	1.02	-0.22	-1.19	-1.94	-2.78	-3.60
800	-0.96	-0.17	0.23	0.47	0.61	0.71	0.76	0.68	0.42	-0.62	-1.55	-2.24	-3.02	-3.85
900	-1.43	-0.84	-0.46	-0.24	-0.12	-0.19	-0.28	-0.38	-0.55	-1.08	-1.88	-2.64	-3.30	-4.11
1000	-1.78	-1.32	-1.01	-0.80	-0.71	-0.80	-0.96	-1.14	-1.25	-1.56	-2.20	-2.85	-3.54	-4.24
1100	-2.05	-1.68	-1.44	-1.27	-1.18	-1.24	-1.43	-1.67	-1.83	-2.05	-2.47	-3.02	-3.65	-4.34
1200	-2.28	-1.97	-1.79	-1.66	-1.56	-1.60	-1.80	-2.07	-2.25	-2.47	-2.79	-3.26	-3.71	-4.25
1300	-2.45	-2.19	-2.08	-1.98	-1.87	-1.89	-2.09	-2.33	-2.53	-2.82	-3.14	-3.47	-3.77	-4.15
1400	-2.61	-2.39	-2.29	-2.23	-2.12	-2.13	-2.32	-2.58	-2.77	-3.05	-3.34	-3.60	-3.85	-4.09

TABLE IV. INVERSION POINTS ($\mu = 0$) FOR CARBON DIOXIDE

Temperature, °C.	Pressure, Bars
100	654
150	776
200	828
250	866
300	881
350	876
400	871
450	862
500	844
600	660
700	446
800	366
900	285
1000	181

and the isochoric heat capacity, C_V, from

$$C_P - C_V = \frac{-T\left[\frac{\partial(PV)}{\partial T}\right]_P^2}{P\left[\frac{\partial(PV)}{\partial P}\right]_T - PV} \qquad (6)$$

and

$$C_V = C_P - (C_P - C_V) \qquad (7)$$

The units of pressure, temperature, and volume are respectively bars, °K., and Amagat units. The conversion factor for PV in bar-Amagat units to calories/mole is 531.97, the same as that used previously (4).

The partial derivation of PV with respect to P was obtained by the same combination of numerical and graphical treatment (4, 6) used to obtain the derivative with respect to T. Since, for a considerable portion of the isotherms, PV is a nearly linear function of P, the same maximum error estimate as that of the previous work was used: 0.2% in PV, and 2% in the first derivative.

Table III contains the Joule-Thomson coefficient as a function of temperature and pressure; Table IV, the inversion data for $\mu = 0$, obtained graphically from the data of Table III. Tables V and VI contain the difference in heat capacities and the isochoric heat capacity, respectively, as functions of pressure and temperature.

DISCUSSION

In the region of overlap (up to 150° C.), the values of μ agree well with those of DeGroot and Michels (1). The largest difference on the two isotherms was 0.011 degrees/bar (8%), and the isobaric plots joined smoothly with the DeGroot and Michels data. The inversion curve of Table II also joins smoothly with the DeGroot and Michels data while the points at 100° and 150° C. are reproduced to 0.5% and 0.1% P, respectively.

The values of (C_P-C_V) at 100° C. generally agree well with those of Michels and DeGroot (3). The differences are large at 200 and 250 bars (6.8 and 3.3%), a region where both the isothermal and isobaric PV values show the greatest departure from linear behavior. The 150° C. values differ in the range from 250 to 500 bars, but this is due to the different values of derivatives used in the two computations (4, 6).

The C_V values, compared to those of Michels and DeGroot (3) at 100° and 150° C., show the same relative behavior as the corresponding set of C_P values: the isotherms of Table VI roughly parallel those of Equation 3 and the values may differ by 1 cal./mole-degree. For isobars, a smooth join to the Michels and DeGroot data can be made only by extrapolating these data to 200° or 250° C. A more detailed discussion of the comparisons in the region of overlap has been given (5).

The remarks (4) on error estimates and regions of probably accuracy are all applicable to the present results. The maximum error for each of the present functions

TABLE V. DIFFERENCE OF THE HEAT CAPACITIES FOR CARBON DIOXIDE AS A FUNCTION OF TEMPERATURE AND PRESSURE

C_P-C_V, Cal./Mole-Degree

Pressure, Bars	Temperature, °C.													
	100	150	200	250	300	350	400	450	500	600	700	800	900	1000
50	3.69	3.04	2.71	2.50	2.38	2.28	2.22	2.17	2.15	2.11	2.09	2.07	2.06	2.06
100	7.37	4.51	3.51	3.04	2.76	2.57	2.45	2.36	2.30	2.22	2.16	2.12	2.10	2.08
150	12.80	6.43	4.41	3.66	3.23	2.92	2.70	2.54	2.44	2.32	2.23	2.18	2.14	2.11
200	14.08	7.95	5.39	4.22	3.59	3.16	2.85	2.67	2.55	2.41	2.30	2.24	2.19	2.15
250	13.19	8.58	6.13	4.83	4.01	3.45	3.08	2.83	2.68	2.50	2.38	2.29	2.23	2.18
300	12.00	8.69	6.77	5.16	4.30	3.74	3.33	3.03	2.84	2.59	2.44	2.34	2.26	2.20
350	10.80	8.34	6.66	5.53	4.55	3.92	3.49	3.15	2.92	2.63	2.48	2.37	2.28	2.21
400	9.88	8.10	6.62	5.58	4.84	4.04	3.59	3.24	2.99	2.68	2.52	2.39	2.29	2.22
450	9.32	7.75	6.43	5.59	4.92	4.22	3.75	3.42	3.14	2.74	2.53	2.40	2.30	2.22
500	8.83	7.54	6.42	5.66	4.98	4.33	3.88	3.56	3.25	2.82	2.56	2.42	2.30	2.21
600	7.88	7.26	6.31	5.47	4.91	4.40	4.02	3.67	3.36	2.91	2.62	2.45	2.29	2.15
700	7.52	6.85	6.05	5.39	4.83	4.44	4.16	3.83	3.46	2.97	2.67	2.48	2.28	2.11
800	7.16	6.73	5.97	5.34	4.87	4.51	4.19	3.89	3.58	3.04	2.70	2.50	2.28	2.09
900	6.88	6.44	5.90	5.35	4.89	4.45	4.12	3.79	3.49	3.07	2.73	2.47	2.26	2.05
1000	6.61	6.26	5.80	5.34	4.88	4.42	4.05	3.71	3.46	3.08	2.74	2.47	2.24	2.03
1100	6.42	6.07	5.69	5.31	4.85	4.42	4.01	3.65	3.40	3.07	2.75	2.47	2.23	2.01
1200	6.25	5.92	5.61	5.26	4.80	4.37	3.95	3.57	3.34	3.04	2.74	2.43	2.23	2.03
1300	6.11	5.84	5.53	5.17	4.73	4.35	3.90	3.53	3.31	2.97	2.66	2.39	2.23	2.07
1400	5.99	5.77	5.55	5.12	4.62	4.25	3.83	3.45	3.26	2.91	2.61	2.38	2.23	2.09

TABLE VI. ISOCHORIC HEAT CAPACITY FOR CO_2 AS A FUNCTION OF TEMPERATURE AND PRESSURE

(C_V, Cal./Mole-Degree)

Pressure, Bars	Temperature, ° C. 100	150	200	250	300	350	400	450	500	600	700	800	900	1000
50	8.1	8.3	8.6	9.0	9.3	9.6	9.8	10.0	10.3	10.6	10.9	11.2	11.4	11.6
100	8.5	8.6	8.9	9.2	9.5	9.7	9.9	10.1	10.2	10.6	11.0	11.2	11.4	11.6
150	9.1	9.4	9.2	9.2	9.5	9.8	9.9	10.1	10.3	10.7	11.0	11.2	11.4	11.7
200	8.9	9.8	9.3	9.3	9.6	9.9	10.1	10.2	10.3	10.7	11.0	11.2	11.5	11.7
250	9.0	9.9	9.4	9.3	9.7	10.0	10.2	10.3	10.4	10.7	11.0	11.2	11.5	11.7
300	9.2	9.9	9.2	9.5	9.8	10.1	10.2	10.3	10.4	10.7	11.0	11.3	11.5	11.7
350	9.3	9.9	9.6	9.4	9.8	10.2	10.3	10.4	10.4	10.7	11.1	11.3	11.5	11.8
400	9.7	10.0	9.6	9.5	9.8	10.3	10.4	10.5	10.5	10.8	11.1	11.3	11.6	11.8
450	9.7	10.0	9.7	9.6	10.0	10.4	10.4	10.4	10.5	10.8	11.1	11.4	11.6	11.8
500	9.8	10.1	9.6	9.5	10.0	10.5	10.4	10.4	10.5	10.8	11.2	11.4	11.6	11.9
600	10.2	10.0	9.5	9.6	10.2	10.6	10.5	10.5	10.6	10.9	11.2	11.5	11.7	12.0
700	10.1	10.1	9.6	9.5	10.2	10.6	10.5	10.6	10.7	11.1	11.3	11.5	11.9	12.2
800	10.1	10.0	9.6	9.5	10.2	10.5	10.5	10.6	10.8	11.1	11.4	11.6	12.0	12.3
900	10.1	10.1	9.6	9.5	10.1	10.6	10.5	10.7	10.9	11.2	11.5	11.8	12.1	12.5
1000	10.2	10.1	9.6	9.4	10.1	10.6	10.6	10.8	11.0	11.3	11.6	11.9	12.3	12.7
1100	10.2	10.2	9.6	9.4	10.2	10.7	10.7	11.0	11.1	11.4	11.6	12.0	12.4	12.8
1200	10.3	10.2	9.6	9.4	10.2	10.7	10.9	11.1	11.2	11.4	11.7	12.1	12.5	12.9
1300	10.3	10.2	9.6	9.5	10.3	10.8	11.0	11.2	11.3	11.5	11.8	12.2	12.5	12.9
1400	10.3	10.2	9.5	9.5	10.4	10.9	11.1	11.3	11.4	11.6	11.9	12.2	12.6	13.0

varies with T and P. This can be illustrated with estimates for (C_P-C_V).

Region	Est. Max. Error in (C_P-C_V).
1. 450-1400 bars, 100° - 350° C.	12.4%
2. 50-400 bars, 100° -350° C. 450-1400 bars, 400°-1000° C.	4.4
3. 50-400 bars, 400° - 1000° C.	4.1

While C_P-C_V depends on first derivatives as they appear in Equation 6, C_V and μ both depend on second derivatives through C_P (estimated maximum error 0.2 to 8.2%). For all of these functions, the maximum error estimate should be made at the point of interest.

DEFINITIONS AND CONVERSION FACTORS

A.U. = Amagat unit
NTP = 0° C. and 1 atm.
V = volume (A.U.) = volume/volume$_{NTP}$
ρ = density (A.U.) = density/density$_{NTP}$
ρ = V^{-1}
P (A.U.) = 505.883 P (gram/cc.)
P(bars) = 0.98692 P (atm.)
PV(bar-A.U.)=531.97 cal./mole
S(cal./mole-degree) = entropy with zero point at 0° C. and 1 atm.

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