Densities of Compressed Liquid Methane, and the Equation of State*

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Experimental *PVT* data for liquid methane are reported at densities from 1.8 times critical up to the freezing liquid, at temperatures from 91 to 245 K and pressures to 350 bar. A nonanalytic equation of state is adjusted to these and other *PVT* data from ideal gas states to the freezing liquid, at temperatures from the triple point to 400 K.

Key words: Compressed liquid; densities; equation of state; methane; orthobaric densities.

Symbols, Units and Constants

(Subscripts *c* and *t* refer to critical and liquid triple points.)

(Subscripts *g* and *l* refer to saturated vapor and liquid.)

α, b, β, δ	constants in eq (4).
$A, B, C, D,$	density-dependent coefficients of eq (4).
$d,$	density, $d_c = 10.15, d_t = 28.1472$ mol/l.
$l,$	the liter, 1000 cm^3 .
mol,	16.043 grams of methane (carbon 12 scale).
$P,$	pressure, 1 bar = 10^5 N/m^2 , 1 atm = 1.01325 bar.
$P_t =$	0.1159 atm = 0.117 4356 bar,
$P_c =$	45.9566 bar.
$R,$	the gas constant, 8.31434 J/mol·K (carbon 12 scale), $R = 0.0831434$ bar-liter/mol K.
$\rho \equiv$	d/d_t , density reduced at the liquid triple point.
$\sigma \equiv$	d/d_c , density reduced at the critical point.
$T,$	temperature, kelvin on IPTS–1968, $T_t = 90.680, T_c = 190.53$.
$T_s(\rho),$	liquid-vapor coexistence temperature.
$\theta(\rho),$	a locus of temperatures.
$v \equiv 1/d,$	molal volume.
$\omega(\rho, T) \equiv$	$(T - \theta)/(\delta \cdot T_c)$.
$x \equiv T/T_c,$	temperature reduced at the critical point.
$Z \equiv Pv/RT,$	the “compressibility factor”.

1. Introduction

This report gives experimental data and analytical formulations which are needed for the computation of tables of thermodynamic functions. Reviews of thermophysical properties [1, 2]¹ show that densities available for the compressed liquid at low temperatures [3, 4] are not of the precision desired for thermal computations. Quite recently we have formulated available coexistence data [5, 6], and we have measured the melting- and vapor-pressures of methane [7].

We now report experimental *PVT* data for the compressed liquid at densities from $1.8 \cdot \rho_c$ up to the melting line, at pressures to 350 bar. We obtain densities of freezing liquid and of saturated liquid from these data by intersection with the *P(T)* melting line and with the *P(T)* vapor pressure line respectively. Densities of saturated vapor are obtained at intersections of the virial equation of state with the *P(T)* vapor pressure line. The corresponding vapor-liquid saturation temperatures, $T_s(\rho)$, then are represented analytically.

Finally, we develop an equation of state for the entire *P(ρ, T)* surface by use of *PVT* data of several authors, which data cover most of the domain at $T_t < T < 400 \text{ K}$, $P \leq 350 \text{ bar}$.

Temperatures are on the kelvin scale of IPTS–1968 [8]. Pressures are related to the International System by use of the bar, 1 bar = 10^5 Newtons per square meter (N/m^2).

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¹ Figures in brackets indicate the literature references at the end of this paper.

2. Densities of the Compressed Liquid

Methane from a commercial supplier is the same lot used for $P(T)$ measurements on the two-phase boundaries [7]. It was specified to be 99.99 percent pure, the principal impurities being N_2 , CO_2 , and C_2H_6 . Independent mass-spectral analysis yields the report of table A.

The apparatus is that developed for hydrogen [9], as modified for oxygen [10] and for fluorine [11]. We have used volumetric calibrations of the latter work

TABLE A. Analysis of the methane sample

Ethane	65 ppm*
Oxygen.....	22-60 ppm
Nitrogen	120-175 ppm
Minimum methane.....	99.97 percent

* Parts per million.

[12]. For methane, the virial equation and a preliminary equation of state are used to find amounts in the gasometer and in nuisance volumes.

Uncertainty in the determination of density is at most 0.1 percent, as noted in [9]. This figure is an accumulation of errors for the total amount of sample, for the amount in capillary tube and null diaphragm, and for the temperature- and pressure-dependent volume of the pipet.

Our PVT data for compressed liquid methane are given in table 1 along experimental pseudo-isochores, arranged in the order of increasing densities. The first column gives our experimental sequence; the second gives density in mol/l; the third is temperature; and the fourth is observed pressure. Additional columns in this and following tables (2, 3, and 4) are discussed below. These data overlap those of Vennix [13] at $1.8 < \rho/\rho_c < 2.2$, and extend up to the melting line.

TABLE 1. NBS densities for compressed liquid methane

ID	MOL/L	T, K	P, BAR	P, CALC	P. PCT	D, PCT
1	10.150	190.530	45.957	45.957	-0.00	
2601	18.384	176.000	32.172	31.403	2.45	-0.22
2602	18.357	180.000	50.437	49.912	1.05	-0.13
2603	18.332	184.000	68.691	68.387	0.44	-0.07
2604	18.307	188.000	86.906	86.781	0.14	-0.03
2605	18.281	192.000	105.089	105.058	0.03	-0.01
2606	18.256	196.000	123.227	123.266	-0.03	0.01
2607	18.232	200.000	141.311	141.405	-0.07	0.02
2608	18.203	205.000	163.860	163.972	-0.07	0.02
2609	18.175	210.000	186.312	186.418	-0.06	0.01
2610	18.150	215.000	208.687	208.828	-0.07	0.02
2611	18.127	220.000	231.002	231.177	-0.08	0.02
2612	18.106	225.000	253.237	253.478	-0.10	0.03
2613	18.086	230.000	275.393	275.691	-0.11	0.03
2614	18.068	235.000	297.479	297.875	-0.13	0.04
2615	18.052	240.000	319.488	320.043	-0.17	0.05
2616	18.036	245.000	341.402	342.090	-0.20	0.06
2501	19.487	170.000	26.367	25.435	3.66	-0.17
2502	19.456	174.000	47.743	47.023	1.53	-0.12
2503	19.427	178.000	69.007	68.507	0.73	-0.08
2504	19.398	182.000	90.117	89.829	0.32	-0.04
2505	19.369	186.000	111.128	110.984	0.13	-0.02
2506	19.340	190.000	132.061	131.970	0.07	-0.01
2507	19.313	194.000	152.913	152.873	0.03	-0.00
2508	19.288	198.000	173.668	173.707	-0.02	0.00
2509	19.264	202.000	194.349	194.436	-0.04	0.01
2510	19.247	205.000	209.838	209.936	-0.05	0.01
2511	19.221	210.000	235.576	235.715	-0.06	0.01
2512	19.197	215.000	261.206	261.396	-0.07	0.02
2513	19.176	220.000	286.762	287.057	-0.10	0.03
2514	19.156	225.000	312.214	312.594	-0.12	0.03
2515	19.138	230.000	337.542	338.084	-0.16	0.04
2401	20.425	164.000	20.288	19.657	3.21	-0.08
2402	20.389	168.000	44.689	44.077	1.39	-0.07
2403	20.357	172.000	68.823	68.407	0.61	-0.05
2404	20.324	176.000	92.700	92.447	0.27	-0.03

TABLE 1. *NBS densities for compressed liquid methane—Continued*

ID	MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
2405	20.292	180.000	116.390	116.290	0.09	−0.01
2406	20.260	184.000	139.966	139.892	0.05	−0.01
2407	20.231	188.000	163.418	163.421	−0.00	0.00
2408	20.206	192.000	186.776	186.963	−0.10	0.02
2409	20.178	196.000	210.084	210.122	−0.02	0.00
2410	20.155	200.000	233.321	233.387	−0.03	0.01
2411	20.134	204.000	256.494	256.599	−0.04	0.01
2412	20.115	208.000	279.599	279.775	−0.06	0.01
2413	20.097	212.000	302.629	302.860	−0.08	0.02
2414	20.080	216.000	325.569	325.862	−0.09	0.02
2415	20.065	220.000	348.434	348.867	−0.12	0.03
2301	21.371	158.000	19.836	19.616	1.12	−0.02
2302	21.332	162.000	47.537	47.203	0.71	−0.03
2303	21.294	166.000	74.747	74.479	0.36	−0.02
2304	21.258	170.000	101.595	101.522	0.07	−0.01
2305	21.223	174.000	128.287	128.293	−0.00	0.00
2306	21.189	178.000	154.807	154.806	0.00	−0.00
2307	21.158	182.000	181.216	181.214	0.00	−0.00
2308	21.129	186.000	207.556	207.477	0.04	−0.01
2309	21.103	190.000	233.818	233.691	0.05	−0.01
2310	21.080	194.000	260.026	259.888	0.05	−0.01
2311	21.059	198.000	286.118	286.015	0.04	−0.01
2312	21.040	202.000	312.140	312.093	0.02	−0.00
2313	21.022	206.000	338.043	338.053	−0.00	0.00
2201	22.125	152.000	14.593	15.002	−2.73	0.03
2202	22.080	156.000	45.088	45.142	−0.12	0.00
2203	22.040	160.000	74.923	75.141	−0.29	0.01
2204	22.001	164.000	104.403	104.772	−0.35	0.02
2205	21.962	168.000	133.692	133.981	−0.22	0.02
2206	21.929	172.000	162.772	163.249	−0.29	0.03
2207	21.892	176.000	191.756	191.825	−0.04	0.00
2208	21.862	180.000	220.648	220.612	0.02	−0.00
2209	21.836	184.000	249.520	249.420	0.04	−0.01
2210	21.812	188.000	278.308	278.109	0.07	−0.01
2211	21.791	192.000	307.015	306.799	0.07	−0.01
2212	21.772	196.000	335.575	335.425	0.04	−0.01
2101	22.873	146.000	13.127	14.032	−6.45	0.05
2102	22.824	150.000	46.703	46.959	−0.55	0.01
2103	22.782	154.000	79.462	79.859	−0.50	0.02
2104	22.739	158.000	111.736	112.134	−0.36	0.02
2105	22.698	162.000	143.810	144.060	−0.17	0.01
2106	22.660	166.000	175.712	175.764	−0.03	0.00
2107	22.626	170.000	207.555	207.387	0.08	−0.01
2108	22.596	174.000	239.330	238.979	0.15	−0.02
2109	22.570	178.000	271.112	270.591	0.19	−0.02
2110	22.546	182.000	302.767	302.060	0.23	−0.03
2111	22.525	186.000	334.282	333.523	0.23	−0.03
2001	23.570	140.000	12.262	13.567	−9.62	0.06
2002	23.518	144.000	48.910	49.337	−0.87	0.02
2003	23.472	148.000	84.500	84.959	−0.54	0.02
2004	23.426	152.000	119.526	119.919	−0.33	0.02
2005	23.383	156.000	154.350	154.555	−0.13	0.01
2006	23.343	160.000	189.067	188.918	0.08	−0.01
2007	23.308	164.000	223.762	223.280	0.22	−0.02
2008	23.278	168.000	258.440	257.710	0.28	−0.03
2009	23.252	172.000	293.040	292.156	0.30	−0.03
2010	23.228	176.000	327.578	326.431	0.35	−0.04
1901	24.183	134.000	6.861	8.975	−23.55	0.08
1902	24.125	138.000	46.383	47.136	−1.60	0.03

TABLE 1. *NBS densities for compressed liquid methane—Continued*

ID	MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
1903	24.076	142.000	84.630	85.409	−0.91	0.03
1904	24.027	146.000	122.240	122.896	−0.53	0.02
1905	23.981	150.000	159.656	159.984	−0.20	0.01
1906	23.940	154.000	197.040	196.975	0.03	−0.00
1801	24.174	134.000	5.841	8.040	−27.35	0.09
1802	24.141	136.000	25.770	26.798	−3.84	0.04
1803	24.115	138.000	45.258	46.066	−1.75	0.03
1804	24.090	140.000	64.512	65.231	−1.10	0.03
1805	24.066	142.000	83.348	84.303	−1.13	0.04
1806	24.042	144.000	102.134	103.182	−1.02	0.04
1807	24.017	146.000	120.944	121.757	−0.67	0.03
1808	23.994	148.000	139.702	140.373	−0.48	0.02
1809	23.971	150.000	158.374	158.811	−0.28	0.02
1810	23.950	152.000	177.053	177.312	−0.15	0.01
1811	23.931	154.000	195.747	195.889	−0.07	0.00
1812	23.912	156.000	214.417	214.311	0.05	−0.00
1813	23.893	158.000	232.888	232.581	0.13	−0.01
1814	23.877	160.000	251.636	251.080	0.22	−0.02
1815	23.862	162.000	270.317	269.571	0.28	−0.02
1816	23.849	164.000	288.962	288.191	0.27	−0.02
1817	23.836	166.000	307.694	306.691	0.33	−0.03
1818	23.824	168.000	326.391	325.205	0.36	−0.04
1819	23.812	170.000	344.986	343.606	0.40	−0.04
1701	24.605	130.000	7.286	9.055	−19.54	0.06
1702	24.572	132.000	28.230	28.867	−2.21	0.02
1703	24.546	134.000	48.781	49.241	−0.93	0.02
1704	24.519	136.000	68.894	69.262	−0.53	0.01
1705	24.494	138.000	88.639	89.295	−0.74	0.02
1706	24.469	140.000	108.425	109.110	−0.63	0.02
1707	24.443	142.000	128.176	128.587	−0.32	0.01
1708	24.419	144.000	147.856	148.106	−0.17	0.01
1709	24.396	146.000	167.516	167.554	−0.02	0.00
1710	24.374	148.000	187.222	186.939	0.15	−0.01
1711	24.354	150.000	206.921	206.403	0.25	−0.02
1712	24.335	152.000	226.644	225.827	0.36	−0.03
1713	24.317	154.000	246.119	245.219	0.37	−0.03
1714	24.301	156.000	265.906	264.725	0.45	−0.04
1715	24.286	158.000	285.671	284.221	0.51	−0.04
1716	24.273	160.000	305.459	303.856	0.53	−0.05
1717	24.260	162.000	325.155	323.358	0.56	−0.05
1718	24.248	164.000	344.921	342.874	0.60	−0.06
1601	24.996	126.000	4.795	7.075	−32.23	0.07
1602	24.960	128.000	26.740	27.553	−2.95	0.03
1603	24.933	130.000	48.275	48.887	−1.25	0.02
1604	24.905	132.000	69.442	69.831	−0.56	0.01
1605	24.879	134.000	90.206	90.781	−0.63	0.02
1606	24.852	136.000	110.901	111.354	−0.41	0.01
1607	24.826	138.000	131.487	131.823	−0.25	0.01
1608	24.801	140.000	152.046	152.198	−0.10	0.00
1609	24.777	142.000	172.619	172.489	0.08	−0.00
1610	24.754	144.000	193.223	192.707	0.27	−0.01
1611	24.734	146.000	213.859	213.146	0.33	−0.02
1612	24.715	148.000	234.593	233.538	0.45	−0.03
1613	24.714	148.000	234.564	233.395	0.50	−0.03
1614	24.697	150.000	255.294	253.895	0.55	−0.04
1615	24.681	152.000	276.024	274.371	0.60	−0.05
1616	24.666	154.000	296.684	294.833	0.63	−0.05
1617	24.652	156.000	317.346	315.290	0.65	−0.06
1618	24.639	158.000	338.030	335.751	0.68	−0.06

TABLE 1. *NBS densities for compressed liquid methane—Continued*

ID	MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
1501	25.386	122.000	3.482	6.324	-44.94	0.08
1502	25.348	124.000	26.168	27.592	-5.16	0.04
1503	25.320	126.000	48.814	49.922	-2.22	0.03
1504	25.293	128.000	70.363	72.103	-2.41	0.05
1505	25.266	130.000	92.218	94.005	-1.90	0.05
1506	25.239	132.000	114.039	115.637	-1.38	0.04
1507	25.212	134.000	135.786	137.005	-0.89	0.03
1508	25.211	134.000	135.814	136.859	-0.76	0.03
1509	25.184	136.000	157.173	157.971	-0.50	0.02
1510	25.160	138.000	178.801	179.281	-0.27	0.01
1511	25.137	140.000	200.430	200.510	-0.04	0.00
1512	25.116	142.000	222.144	221.822	0.15	-0.01
1513	25.097	144.000	243.865	243.231	0.26	-0.02
1514	25.080	146.000	265.643	264.755	0.34	-0.02
1515	25.064	148.000	287.462	286.251	0.42	-0.03
1516	25.049	150.000	309.282	307.728	0.50	-0.04
1517	25.035	152.000	330.987	329.197	0.54	-0.04
1518	25.022	154.000	352.726	350.667	0.59	-0.05
1401	25.777	118.000	4.740	7.269	-34.80	0.07
1402	25.739	120.000	28.487	29.634	-3.87	0.03
1403	25.710	122.000	51.814	53.002	-2.24	0.03
1404	25.682	124.000	74.303	76.199	-2.49	0.05
1405	25.654	126.000	97.196	99.086	-1.91	0.05
1406	25.625	128.000	120.010	121.516	-1.24	0.04
1407	25.598	130.000	142.846	143.967	-0.78	0.03
1408	25.574	132.000	165.554	166.619	-0.64	0.03
1409	25.550	134.000	188.320	189.008	-0.36	0.02
1410	25.524	136.000	211.062	210.816	0.12	-0.01
1411	25.503	138.000	233.855	233.195	0.28	-0.02
1412	25.503	138.000	233.445	233.195	0.11	-0.01
1413	25.484	140.000	256.331	255.678	0.26	-0.02
1414	25.466	142.000	279.330	278.111	0.44	-0.03
1415	25.450	144.000	302.209	300.677	0.51	-0.04
1416	25.435	146.000	325.227	323.221	0.62	-0.05
1417	25.422	148.000	348.148	345.926	0.64	-0.05
1301	26.142	114.000	4.106	5.811	-29.34	0.04
1302	26.103	116.000	28.896	29.135	-0.82	0.01
1303	26.072	118.000	52.968	53.369	-0.75	0.01
1304	26.044	120.000	76.358	77.737	-1.77	0.03
1305	26.014	122.000	100.162	101.430	-1.25	0.03
1306	25.985	124.000	123.929	124.955	-0.82	0.02
1307	25.956	126.000	147.655	148.158	-0.34	0.01
1308	25.929	128.000	171.338	171.393	-0.03	0.00
1309	25.904	130.000	195.123	194.677	0.23	-0.01
1310	25.881	132.000	218.955	218.030	0.42	-0.02
1311	25.880	132.000	218.534	217.855	0.31	-0.01
1312	25.859	134.000	242.441	241.293	0.48	-0.03
1313	25.840	136.000	266.440	264.837	0.61	-0.03
1314	25.822	138.000	290.474	288.323	0.75	-0.05
1315	25.807	140.000	314.577	312.130	0.78	-0.05
1316	25.792	142.000	338.590	335.726	0.85	-0.06
1201	26.519	110.000	5.935	7.782	-23.73	0.04
1202	26.480	112.000	31.839	32.288	-1.39	0.01
1203	26.449	114.000	56.444	57.777	-2.31	0.03
1204	26.419	116.000	81.054	83.045	-2.40	0.04
1205	26.388	118.000	105.870	107.750	-1.74	0.04
1206	26.357	120.000	130.659	132.083	-1.08	0.03
1207	26.327	122.000	155.400	156.241	-0.54	0.02
1208	26.299	124.000	180.154	180.425	-0.15	0.01

TABLE 1. *NBS densities for compressed liquid methane*—Continued

ID	MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
1209	26.274	126.000	204.975	204.840	0.07	−0.00
1210	26.251	128.000	229.892	229.325	0.25	−0.01
1211	26.230	130.000	254.906	253.899	0.40	−0.02
1212	26.211	132.000	280.025	278.581	0.52	−0.03
1213	26.193	134.000	305.214	303.196	0.67	−0.04
1214	26.192	134.000	304.967	303.002	0.65	−0.04
1215	26.176	136.000	330.185	327.759	0.74	−0.05
1101	26.901	106.000	12.022	12.593	−4.54	0.01
1102	26.864	108.000	38.986	38.731	0.66	−0.00
1103	26.833	110.000	64.591	65.550	−1.46	0.02
1104	26.801	112.000	90.300	91.734	−1.56	0.03
1105	26.768	114.000	116.122	117.294	−1.00	0.02
1106	26.736	116.000	141.871	142.638	−0.54	0.01
1107	26.706	118.000	167.653	167.983	−0.20	0.01
1108	26.679	120.000	193.539	193.550	−0.01	0.00
1109	26.653	122.000	219.542	218.964	0.26	−0.01
1110	26.630	124.000	245.820	244.647	0.48	−0.02
1111	26.631	124.000	245.678	244.851	0.34	−0.02
1112	26.610	126.000	272.049	270.626	0.53	−0.03
1113	26.592	128.000	298.510	296.721	0.60	−0.03
1114	26.574	130.000	325.020	322.534	0.77	−0.04
1115	26.559	132.000	351.423	348.707	0.78	−0.05
1001	27.232	102.000	8.474	9.235	−8.24	0.01
1002	27.192	104.000	36.489	36.050	1.22	−0.01
1003	27.160	106.000	63.034	63.985	−1.49	0.02
1004	27.127	108.000	89.515	91.224	−1.87	0.03
1005	27.093	110.000	116.218	117.781	−1.33	0.03
1006	27.060	112.000	142.937	144.093	−0.80	0.02
1007	27.029	114.000	169.612	170.392	−0.46	0.01
1008	27.001	116.000	196.480	196.915	−0.22	0.01
1009	27.001	116.000	196.471	196.915	−0.23	0.01
1010	26.976	118.000	223.568	223.689	−0.05	0.00
1011	26.952	120.000	250.862	250.311	0.22	−0.01
1012	26.931	122.000	278.278	277.234	0.38	−0.02
1013	26.912	124.000	305.898	304.267	0.54	−0.03
1014	26.895	126.000	333.424	331.430	0.60	−0.03
901	27.588	98.000	12.437	12.343	0.76	−0.00
902	27.548	100.000	41.407	40.503	2.23	−0.01
903	27.516	102.000	68.696	69.861	−1.67	0.02
904	27.481	104.000	96.270	98.007	−1.77	0.03
905	27.447	106.000	124.002	125.853	−1.47	0.03
906	27.413	108.000	151.755	153.199	−0.94	0.02
907	27.382	110.000	179.649	180.747	−0.61	0.02
908	27.353	112.000	207.794	208.298	−0.24	0.01
909	27.328	114.000	236.148	236.336	−0.08	0.00
910	27.305	116.000	264.752	264.435	0.12	−0.01
911	27.305	116.000	264.894	264.435	0.17	−0.01
912	27.285	118.000	293.612	292.851	0.26	−0.01
913	27.266	120.000	322.446	321.144	0.41	−0.02
801	27.900	94.000	7.513	6.980	7.64	−0.01
802	27.858	96.000	37.517	36.064	4.03	−0.02
803	27.825	98.000	65.517	66.637	−1.68	0.02
804	27.789	100.000	94.061	95.894	−1.91	0.03
805	27.753	102.000	122.725	124.572	−1.48	0.03
806	27.719	104.000	151.383	153.178	−1.17	0.03
807	27.686	106.000	180.222	181.498	−0.70	0.02
808	27.657	108.000	209.351	210.286	−0.44	0.01
809	27.630	110.000	238.728	239.088	−0.15	0.01
810	27.607	112.000	268.394	268.423	−0.01	0.00

TABLE 1. *NBS densities for compressed liquid methane—Continued*

ID	MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
811	27.586	114.000	298.261	297.832	0.14	-0.01
812	27.567	116.000	328.347	327.343	0.31	-0.01
1	28.147	90.680	0.117	0.117	0.00	0.00
601	28.209	92.000	44.123	42.754	3.20	-0.02
602	28.175	94.000	72.852	74.640	-2.40	0.02
603	28.137	96.000	102.543	104.830	-2.18	0.03
604	28.101	98.000	132.353	134.893	-1.88	0.04
605	28.066	100.000	162.180	164.607	-1.47	0.03
606	28.066	100.000	162.190	164.607	-1.47	0.03
607	28.034	102.000	192.243	194.518	-1.17	0.03
608	28.004	104.000	222.687	224.401	-0.76	0.02
609	27.978	106.000	253.551	254.808	-0.49	0.02
610	27.955	108.000	284.641	285.515	-0.31	0.01
611	27.935	110.000	316.018	316.555	-0.17	0.01
612	27.916	112.000	347.527	347.429	0.03	-0.00
701	28.391	94.000	128.133	131.785	-2.77	0.05
702	28.354	96.000	158.893	162.333	-2.12	0.04
703	28.321	98.000	189.886	193.337	-1.78	0.04
704	28.290	100.000	221.338	224.286	-1.31	0.04
705	28.264	102.000	253.222	256.041	-1.10	0.04
706	28.240	104.000	285.440	287.814	-0.82	0.03
707	28.219	106.000	318.049	319.914	-0.58	0.02
708	28.200	108.000	350.566	352.099	-0.44	0.02
514	28.552	96.500	224.938	228.216	-1.44	0.04
515	28.545	97.000	233.128	236.381	-1.38	0.04
516	28.531	98.000	249.643	252.596	-1.17	0.04
517	28.507	100.000	282.843	285.748	-1.02	0.03
518	28.507	100.000	282.935	285.748	-0.98	0.03
519	28.486	102.000	316.433	319.221	-0.87	0.03
520	28.466	104.000	350.093	352.461	-0.67	0.03

TABLE 2. *Methane densities via the virial equation of [5]*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
0.500	140.000	5.213	5.221	-0.14	0.16
0.500	145.000	5.443	5.448	-0.09	0.10
0.500	150.000	5.670	5.673	-0.05	0.06
0.500	155.000	5.896	5.898	-0.03	0.03
0.500	160.000	6.120	6.121	-0.01	0.01
0.500	165.000	6.344	6.344	-0.00	0.00
0.500	170.000	6.566	6.566	0.00	-0.00
0.500	175.000	6.788	6.787	0.01	-0.01
0.500	180.000	7.009	7.008	0.01	-0.01
0.500	185.000	7.229	7.228	0.01	-0.01
0.500	190.000	7.448	7.448	0.01	-0.01
0.500	195.000	7.668	7.667	0.01	-0.01
0.500	200.000	7.887	7.886	0.00	-0.00
0.500	205.000	8.105	8.105	0.00	-0.00
0.500	210.000	8.323	8.323	-0.00	0.00
0.500	215.000	8.541	8.541	-0.00	0.00
0.500	220.000	8.758	8.759	-0.00	0.00
0.500	225.000	8.976	8.976	-0.01	0.01
0.500	230.000	9.193	9.193	-0.01	0.01
0.500	235.000	9.409	9.410	-0.01	0.01
0.500	240.000	9.626	9.627	-0.01	0.01
0.500	245.000	9.842	9.844	-0.01	0.01
0.500	250.000	10.059	10.060	-0.01	0.01
0.500	255.000	10.275	10.276	-0.01	0.01
0.500	260.000	10.491	10.492	-0.01	0.01
0.500	265.000	10.707	10.708	-0.01	0.01
0.500	270.000	10.923	10.924	-0.01	0.01
1.000	150.000	10.230	10.247	-0.16	0.21
1.000	155.000	10.723	10.731	-0.08	0.09
1.000	160.000	11.209	11.211	-0.02	0.02
1.000	165.000	11.689	11.687	0.02	-0.02
1.000	170.000	12.165	12.160	0.04	-0.05
1.000	175.000	12.636	12.630	0.05	-0.06
1.000	180.000	13.105	13.097	0.06	-0.07
1.000	185.000	13.570	13.563	0.06	-0.06
1.000	190.000	14.033	14.026	0.05	-0.06
1.000	195.000	14.494	14.488	0.05	-0.05
1.000	200.000	14.954	14.948	0.04	-0.04
1.000	205.000	15.411	15.406	0.03	-0.04
1.000	210.000	15.867	15.864	0.02	-0.03
1.000	215.000	16.322	16.320	0.02	-0.02
1.000	220.000	16.776	16.774	0.01	-0.01
1.000	225.000	17.229	17.228	0.00	-0.01
1.000	230.000	17.681	17.681	-0.00	0.00
1.000	235.000	18.132	18.133	-0.01	0.01
1.000	240.000	18.583	18.585	-0.01	0.01
1.000	245.000	19.032	19.035	-0.01	0.02
1.000	250.000	19.481	19.485	-0.02	0.02
1.000	255.000	19.930	19.934	-0.02	0.02
1.000	260.000	20.378	20.382	-0.02	0.03
1.000	265.000	20.825	20.830	-0.03	0.03
1.000	270.000	21.272	21.278	-0.03	0.03
1.500	160.000	15.310	15.319	-0.06	0.09
1.500	165.000	16.084	16.081	0.02	-0.03
1.500	170.000	16.847	16.834	0.08	-0.10
1.500	175.000	17.599	17.580	0.11	-0.14
1.500	180.000	18.343	18.321	0.12	-0.15
1.500	185.000	19.079	19.056	0.12	-0.15
1.500	190.000	19.809	19.787	0.11	-0.14

TABLE 2. *Methane densities via the virial equation of [5]—Continued*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
1.500	195.000	20.535	20.514	0.10	−0.12
1.500	200.000	21.256	21.237	0.09	−0.11
1.500	205.000	21.973	21.956	0.08	−0.09
1.500	210.000	22.686	22.672	0.06	−0.07
1.500	215.000	23.397	23.386	0.05	−0.06
1.500	220.000	24.106	24.097	0.03	−0.04
1.500	225.000	24.812	24.806	0.02	−0.02
1.500	230.000	25.516	25.513	0.01	−0.01
1.500	235.000	26.218	26.218	0.00	−0.00
1.500	240.000	26.919	26.921	−0.01	0.01
1.500	245.000	27.618	27.622	−0.02	0.02
1.500	250.000	28.315	28.322	−0.02	0.03
1.500	255.000	29.012	29.021	−0.03	0.03
1.500	260.000	29.707	29.718	−0.04	0.04
1.500	265.000	30.401	30.414	−0.04	0.04
1.500	270.000	31.094	31.108	−0.04	0.05
2.000	170.000	20.664	20.639	0.12	−0.19
2.000	175.000	21.729	21.691	0.18	−0.26
2.000	180.000	22.776	22.731	0.20	−0.28
2.000	185.000	23.810	23.761	0.21	−0.28
2.000	190.000	24.831	24.782	0.20	−0.26
2.000	195.000	25.843	25.796	0.18	−0.24
2.000	200.000	26.847	26.803	0.16	−0.21
2.000	205.000	27.843	27.804	0.14	−0.18
2.000	210.000	28.833	28.800	0.12	−0.14
2.000	215.000	29.818	29.790	0.09	−0.11
2.000	220.000	30.798	30.777	0.07	−0.09
2.000	225.000	31.775	31.759	0.05	−0.06
2.000	230.000	32.747	32.737	0.03	−0.04
2.000	235.000	33.717	33.712	0.01	−0.02
2.000	240.000	34.683	34.684	−0.00	0.00
2.000	245.000	35.647	35.653	−0.02	0.02
2.000	250.000	36.609	36.619	−0.03	0.03
2.000	255.000	37.568	37.583	−0.04	0.04
2.000	260.000	38.526	38.544	−0.05	0.05
2.000	265.000	39.482	39.504	−0.06	0.06
2.000	270.000	40.436	40.461	−0.06	0.07

TABLE 3. *Methane densities of Vennix [13]*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
2.560	172.527	24.660	24.653	0.03	-0.06
2.560	174.691	25.283	25.269	0.05	-0.09
2.559	177.203	25.994	25.976	0.07	-0.12
2.559	183.176	27.666	27.642	0.09	-0.14
2.559	190.532	29.676	29.664	0.04	-0.06
2.558	191.849	30.038	30.016	0.07	-0.10
2.556	203.084	33.048	33.036	0.04	-0.05
2.555	213.041	35.672	35.668	0.01	-0.02
2.555	217.864	36.931	36.930	0.00	-0.00
2.554	223.831	38.481	38.483	-0.00	0.00
2.553	233.546	40.990	40.989	0.00	-0.00
2.552	239.797	42.590	42.593	-0.01	0.01
2.551	252.833	45.897	45.910	-0.03	0.03
2.550	263.399	48.559	48.575	-0.03	0.04
2.548	273.380	51.058	51.074	-0.03	0.04
6.469	190.429	44.720	44.545	0.39	-2.53
6.471	190.532	44.814	44.641	0.39	-2.47
6.464	208.574	60.270	60.264	0.01	-0.02
6.459	223.234	72.346	72.419	-0.10	0.17
6.456	234.440	81.433	81.539	-0.13	0.20
6.453	243.733	88.913	89.016	-0.12	0.16
6.453	243.773	88.939	89.048	-0.12	0.17
6.451	251.376	95.018	95.119	-0.11	0.14
6.447	262.190	103.601	103.700	-0.10	0.12
6.444	272.155	111.478	111.550	-0.06	0.08
6.444	272.185	111.494	111.573	-0.07	0.08
7.235	190.052	44.989	44.798	0.43	-5.39
7.237	190.532	45.493	45.304	0.42	-4.35
7.235	190.750	45.710	45.532	0.39	-3.80
7.237	191.032	46.001	45.827	0.38	-3.40
7.234	193.325	48.336	48.192	0.30	-1.76
7.233	197.737	52.722	52.644	0.15	-0.57
7.231	202.753	57.627	57.604	0.04	-0.11
7.229	208.224	62.909	62.934	-0.04	0.10
7.228	212.165	66.689	66.736	-0.07	0.15
7.226	217.136	71.421	71.494	-0.10	0.20
7.224	222.926	76.909	76.995	-0.11	0.20
7.222	230.050	83.614	83.713	-0.12	0.19
7.219	237.336	90.432	90.536	-0.11	0.17
7.217	242.709	95.434	95.540	-0.11	0.15
7.215	248.444	100.757	100.861	-0.10	0.14
7.215	250.194	102.376	102.481	-0.10	0.13
7.214	253.445	105.378	105.483	-0.10	0.13
7.212	258.642	110.172	110.270	-0.09	0.11
7.210	263.050	114.229	114.323	-0.08	0.10
7.209	268.301	119.049	119.134	-0.07	0.09
7.207	273.171	123.504	123.581	-0.06	0.07
9.844	190.532	45.870	45.958	-0.19	12.43
9.844	191.032	46.579	46.685	-0.23	9.45
9.840	191.551	47.318	47.434	-0.25	7.18
9.840	192.938	49.282	49.431	-0.30	4.43
9.839	195.243	52.563	52.742	-0.34	2.62
9.838	197.562	55.870	56.069	-0.36	1.87
9.837	200.411	59.977	60.154	-0.29	1.13
9.835	202.829	63.417	63.620	-0.32	1.01
9.834	206.370	68.503	68.695	-0.28	0.72
9.830	213.503	78.771	78.921	-0.19	0.37
9.825	223.647	93.389	93.464	-0.08	0.12
9.819	236.398	111.767	111.738	0.03	-0.03

TABLE 3. Methane densities of Vennix [13]—Continued

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
9.814	248.147	128.674	128.567	0.08	−0.09
9.811	255.163	138.749	138.596	0.11	−0.12
9.802	273.167	164.504	164.289	0.13	−0.13
10.220	190.532	45.875	45.960	−0.18	16.32
10.219	191.032	46.607	46.705	−0.21	11.70
10.216	190.839	46.342	46.417	−0.16	11.88
10.216	191.040	46.618	46.717	−0.21	11.72
10.216	191.229	46.900	46.999	−0.21	9.98
10.216	191.428	47.188	47.296	−0.23	9.07
10.216	191.820	47.762	47.881	−0.25	7.34
10.216	192.076	48.131	48.264	−0.27	6.76
10.215	193.522	50.263	50.427	−0.32	4.00
10.214	195.158	52.700	52.877	−0.33	2.60
10.213	197.926	56.836	57.030	−0.34	1.64
10.212	200.575	60.814	61.011	−0.32	1.17
10.210	204.037	66.036	66.221	−0.28	0.78
10.208	207.855	71.799	71.978	−0.25	0.56
10.208	207.855	71.833	71.978	−0.20	0.46
10.206	213.044	79.691	79.814	−0.15	0.29
10.196	233.386	110.688	110.614	0.07	−0.08
10.186	252.887	140.387	140.173	0.15	−0.16
10.176	273.016	170.925	170.615	0.18	−0.17
10.176	273.058	170.987	170.679	0.18	−0.17
11.163	190.532	45.834	46.006	−0.37	30.29
11.162	191.032	46.643	46.808	−0.35	18.86
11.158	191.848	47.983	48.136	−0.32	5.62
11.158	191.873	48.009	48.177	−0.35	6.32
11.158	193.248	50.248	50.442	−0.39	3.48
11.157	195.110	53.340	53.540	−0.37	2.07
11.156	197.300	56.992	57.211	−0.38	1.50
11.155	199.216	60.228	60.441	−0.35	1.12
11.154	200.901	63.092	63.294	−0.32	0.87
11.153	203.064	66.782	66.968	−0.28	0.65
11.150	207.564	74.518	74.650	−0.18	0.33
11.147	213.197	84.266	84.322	−0.07	0.10
11.147	213.204	84.282	84.334	−0.06	0.10
11.147	213.212	84.293	84.348	−0.07	0.10
11.141	223.184	101.660	101.576	0.08	−0.10
11.136	233.161	119.122	118.904	0.18	−0.20
11.131	243.137	136.601	136.272	0.24	−0.24
11.126	253.153	154.123	153.739	0.25	−0.23
11.120	263.124	171.554	171.120	0.25	−0.22
11.115	273.092	188.977	188.493	0.26	−0.22
11.115	273.150	188.927	188.594	0.18	−0.15
11.771	190.532	45.823	46.135	−0.68	38.23
11.771	191.032	46.701	46.992	−0.62	16.17
11.767	192.498	49.295	49.551	−0.52	3.70
11.765	195.840	55.256	55.516	−0.47	1.65
11.764	198.182	59.511	59.756	−0.41	1.10
11.760	203.434	69.192	69.378	−0.27	0.50
11.755	212.034	85.308	85.352	−0.05	0.07
11.755	212.035	85.310	85.354	−0.05	0.07
11.749	222.632	105.407	105.264	0.14	−0.15
11.744	233.402	125.956	125.658	0.24	−0.23
11.744	233.403	125.973	125.660	0.25	−0.24
11.741	237.033	132.922	132.549	0.28	−0.26
11.741	237.034	132.920	132.551	0.28	−0.26
11.737	243.378	145.053	144.614	0.30	−0.27
11.737	243.381	145.050	144.620	0.30	−0.27

TABLE 3. *Methane densities of Vennix [13]—Continued*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
11.732	253.284	163.987	163.492	0.30	-0.25
11.726	263.449	183.402	182.854	0.30	-0.24
11.724	268.300	192.683	192.101	0.30	-0.24
11.724	268.300	192.678	192.101	0.30	-0.24
11.721	272.694	201.050	200.469	0.29	-0.23
11.721	272.695	201.049	200.471	0.29	-0.22
11.721	272.698	201.046	200.476	0.28	-0.22
12.873	190.032	45.236	45.783	-1.20	11.00
12.872	191.032	47.247	47.773	-1.10	5.03
12.873	190.532	46.239	46.774	-1.15	6.77
12.868	190.703	46.599	47.111	-1.09	5.71
12.868	191.454	48.097	48.616	-1.07	4.21
12.868	192.397	49.969	50.523	-1.10	3.45
12.865	196.505	58.521	58.995	-0.80	1.47
12.861	203.573	73.642	73.948	-0.41	0.51
12.857	209.295	86.110	86.266	-0.18	0.19
12.851	218.622	106.682	106.607	0.07	-0.06
12.845	228.103	127.755	127.493	0.21	-0.17
12.839	238.550	151.093	150.664	0.28	-0.21
12.834	245.920	167.546	167.060	0.29	-0.21
12.829	252.972	183.347	182.778	0.31	-0.22
12.825	260.108	199.300	198.695	0.30	-0.21
12.821	267.312	215.373	214.767	0.28	-0.19
12.816	274.151	230.576	230.010	0.25	-0.16
13.756	188.969	43.856	44.457	-1.35	4.64
13.756	189.258	44.502	45.108	-1.34	4.05
13.756	189.767	45.639	46.262	-1.35	3.43
13.759	190.032	46.240	46.872	-1.35	3.19
13.755	190.172	46.549	47.183	-1.35	3.09
13.759	191.032	48.523	49.161	-1.30	2.50
13.755	190.447	47.177	47.812	-1.33	2.87
13.759	190.532	47.379	48.014	-1.32	2.80
13.755	190.738	47.840	48.478	-1.32	2.68
13.755	191.075	48.615	49.251	-1.29	2.48
13.753	192.892	52.817	53.453	-1.19	1.80
13.752	195.048	57.893	58.501	-1.04	1.31
13.752	195.065	57.928	58.542	-1.05	1.32
13.751	197.100	62.787	63.356	-0.90	1.00
13.749	200.010	69.812	70.306	-0.70	0.69
13.746	203.322	77.904	78.293	-0.50	0.44
13.744	207.197	87.439	87.726	-0.33	0.27
13.740	213.323	102.706	102.776	-0.07	0.05
13.733	222.792	126.432	126.292	0.11	-0.08
13.730	227.846	139.174	138.931	0.17	-0.12
13.727	233.272	152.884	152.544	0.22	-0.14
13.723	238.508	166.109	165.711	0.24	-0.15
13.720	242.985	177.429	176.987	0.25	-0.16
13.716	248.766	192.026	191.574	0.24	-0.15
13.713	253.111	203.005	202.554	0.22	-0.14
13.710	258.314	216.145	215.688	0.21	-0.13
13.707	262.932	227.811	227.350	0.20	-0.12
13.703	267.819	240.117	239.690	0.18	-0.11
13.703	267.886	240.288	239.861	0.18	-0.11
13.700	273.153	253.551	253.145	0.16	-0.09
14.976	187.649	43.274	43.891	-1.41	1.34
14.975	188.927	46.771	47.426	-1.38	1.18
14.978	190.532	51.216	51.918	-1.35	1.05
14.973	191.453	53.786	54.477	-1.27	0.94
14.971	194.804	63.256	63.941	-1.07	0.71

TABLE 3. *Methane densities of Vennix [13]—Continued*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
14.967	199.611	77.104	77.688	-0.75	0.45
14.965	203.054	87.135	87.635	-0.57	0.33
14.961	207.627	100.574	100.948	-0.37	0.20
14.958	212.935	116.265	116.512	-0.21	0.11
14.951	221.360	141.310	141.395	-0.06	0.03
14.946	228.637	163.016	163.004	0.01	-0.00
14.940	236.599	186.801	186.739	0.03	-0.02
14.934	245.086	212.140	212.082	0.03	-0.01
14.928	253.068	235.968	235.924	0.02	-0.01
14.922	260.836	259.036	259.131	-0.04	0.02
14.917	268.824	282.716	282.976	-0.09	0.05
14.912	275.154	301.472	301.821	-0.12	0.06
16.529	183.351	38.252	38.638	-1.00	0.30
16.527	185.267	44.884	45.439	-1.22	0.38
16.524	189.259	58.970	59.716	-1.25	0.41
16.528	190.532	63.513	64.353	-1.31	0.43
16.520	194.419	77.509	78.329	-1.05	0.35
16.517	198.420	91.963	92.864	-0.97	0.33
16.514	201.044	101.638	102.427	-0.77	0.27
16.509	207.770	126.173	127.056	-0.70	0.25
16.504	213.668	147.882	148.744	-0.58	0.21
16.496	222.893	181.824	182.777	-0.52	0.20
16.488	232.812	218.350	219.431	-0.49	0.19
16.481	241.295	249.578	250.780	-0.48	0.19
16.471	254.531	298.027	299.605	-0.53	0.21
16.464	261.826	324.594	326.421	-0.56	0.23
16.459	267.883	346.584	348.640	-0.59	0.24
16.455	272.981	364.997	367.288	-0.62	0.26
17.570	179.140	33.044	32.888	0.48	-0.07
17.570	179.830	35.849	35.772	0.22	-0.03
17.568	181.008	40.651	40.700	-0.12	0.02
17.565	184.441	54.773	55.111	-0.61	0.12
17.566	190.532	80.090	80.938	-1.05	0.24
17.555	196.384	104.601	105.638	-0.98	0.25
17.551	200.537	122.244	123.296	-0.85	0.23
17.544	208.822	157.426	158.617	-0.75	0.22
17.537	217.044	192.276	193.684	-0.73	0.22
17.530	225.022	225.974	227.709	-0.76	0.24
17.522	233.079	259.963	261.996	-0.78	0.25
17.515	240.996	293.223	295.632	-0.81	0.27
17.507	250.735	333.924	336.853	-0.87	0.30
17.500	258.646	366.598	370.211	-0.98	0.35
17.493	266.750	400.092	404.263	-1.03	0.37
17.486	274.303	431.136	435.827	-1.08	0.39
18.495	182.834	65.518	66.743	-1.84	0.27
18.495	182.834	65.491	66.743	-1.87	0.28
18.502	175.629	31.376	31.857	-1.51	0.13
18.500	178.081	42.935	43.709	-1.77	0.20
18.490	188.292	91.648	93.246	-1.71	0.30
18.494	190.532	102.401	104.296	-1.82	0.34
18.485	193.630	117.303	119.193	-1.59	0.32
18.480	198.667	141.558	143.673	-1.47	0.32
18.476	203.156	163.181	165.489	-1.39	0.32
18.472	208.214	187.511	190.068	-1.35	0.33
18.467	212.424	207.694	210.472	-1.32	0.34
18.462	218.758	238.049	241.163	-1.29	0.35
18.457	223.742	261.867	265.231	-1.27	0.35
18.452	229.135	287.485	291.240	-1.29	0.37
18.448	233.395	307.683	311.741	-1.30	0.38

TABLE 3. *Methane densities of Vennix [13]—Continued*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
18.444	237.607	327.596	331.970	−1.32	0.39
18.439	243.055	353.252	358.014	−1.33	0.40
18.434	248.039	376.587	381.812	−1.37	0.42
18.429	253.126	400.348	405.992	−1.39	0.44
18.420	263.283	447.525	454.082	−1.44	0.47
18.411	272.927	498.737	499.450	−0.14	0.05
20.003	172.566	55.009	57.430	−4.21	0.32
19.997	178.480	90.082	93.134	−3.28	0.36
19.988	186.850	139.761	143.501	−2.61	0.38
19.991	190.532	161.544	165.925	−2.64	0.42
19.979	196.089	194.310	198.830	−2.27	0.40
19.970	204.181	241.785	246.973	−2.10	0.41
19.963	211.525	284.629	290.457	−2.01	0.43
19.955	219.063	328.253	334.799	−1.95	0.44
19.946	227.105	374.341	381.848	−1.97	0.47
19.938	235.300	421.001	429.484	−1.98	0.50
19.929	244.174	470.891	480.637	−2.03	0.53
19.919	253.828	524.859	535.856	−2.05	0.56
19.913	259.343	555.441	567.200	−2.07	0.58
19.905	267.733	601.053	614.570	−2.20	0.63
19.898	274.489	638.125	652.480	−2.20	0.65
21.221	172.766	113.831	119.246	−4.54	0.42
21.216	176.889	142.805	148.646	−3.93	0.42
21.211	181.669	176.336	182.542	−3.40	0.42
21.201	189.783	232.523	239.707	−3.00	0.44
21.207	190.532	237.772	245.506	−3.15	0.47
21.193	197.315	284.387	292.377	−2.73	0.45
21.186	204.169	331.269	339.933	−2.55	0.46
21.176	212.644	388.576	398.246	−2.43	0.48
21.158	228.430	493.464	505.405	−2.36	0.52
21.150	235.778	541.550	554.696	−2.37	0.55
21.138	247.380	616.528	631.777	−2.41	0.59
21.131	252.992	652.311	668.704	−2.45	0.61
22.419	168.753	169.422	177.589	−4.60	0.42
22.405	180.116	262.685	271.707	−3.32	0.41
22.395	188.528	330.450	340.419	−2.93	0.42
22.400	190.532	346.440	357.440	−3.08	0.45
22.385	196.791	396.392	407.118	−2.63	0.42
22.376	204.366	455.919	467.593	−2.50	0.43
22.368	211.255	509.403	522.106	−2.43	0.45
22.360	218.293	563.516	577.319	−2.39	0.46
22.350	226.285	624.075	639.303	−2.38	0.49
22.340	234.420	685.032	701.878	−2.40	0.51

TABLE 4. *Methane densities of Douslin et al. [22]*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
0.750	273.150	16.376	16.377	-0.00	0.01
0.750	298.142	18.020	18.020	0.00	0.00
0.750	303.143	18.347	18.348	-0.00	0.00
0.750	323.140	19.656	19.658	-0.01	0.01
0.750	348.143	21.292	21.292	0.00	-0.00
0.750	373.150	22.925	22.923	0.01	-0.01
0.750	398.160	24.557	24.551	0.03	-0.03
1.000	273.150	21.558	21.559	-0.01	0.01
1.000	298.142	23.786	23.787	-0.01	0.01
1.000	303.143	24.232	24.232	0.00	-0.00
1.000	323.140	26.006	26.007	-0.00	0.00
1.000	348.143	28.221	28.219	0.01	-0.01
1.000	373.150	30.431	30.425	0.02	-0.02
1.000	398.160	32.637	32.627	0.03	-0.03
1.500	273.150	31.539	31.545	-0.02	0.02
1.500	298.142	34.993	34.999	-0.02	0.02
1.500	303.143	35.685	35.688	-0.01	0.01
1.500	323.140	38.427	38.434	-0.02	0.02
1.500	348.143	41.852	41.853	-0.00	0.00
1.500	373.150	45.267	45.260	0.02	-0.02
1.500	398.160	48.676	48.656	0.04	-0.04
2.000	273.150	41.053	41.063	-0.03	0.03
2.000	298.142	45.804	45.817	-0.03	0.03
2.000	303.143	46.753	46.764	-0.02	0.03
2.000	323.140	50.530	50.538	-0.01	0.02
2.000	348.143	55.222	55.232	-0.02	0.02
2.000	373.150	59.920	59.905	0.02	-0.03
2.000	398.160	64.582	64.561	0.03	-0.03
2.500	273.150	50.139	50.158	-0.04	0.04
2.500	298.142	56.263	56.286	-0.04	0.04
2.500	303.143	57.485	57.506	-0.04	0.04
2.500	323.140	62.343	62.364	-0.03	0.04
2.500	348.143	68.390	68.403	-0.02	0.02
2.500	373.150	74.424	74.411	0.02	-0.02
2.500	398.160	80.411	80.392	0.02	-0.02
3.000	273.150	58.842	58.875	-0.06	0.06
3.000	298.142	66.415	66.451	-0.05	0.06
3.000	303.143	67.940	67.958	-0.03	0.03
3.000	323.140	73.926	73.958	-0.04	0.05
3.000	348.143	81.391	81.413	-0.03	0.03
3.000	373.150	88.835	88.825	0.01	-0.01
3.000	398.160	96.229	96.201	0.03	-0.03
3.500	273.150	67.222	67.258	-0.05	0.06
3.500	298.142	76.307	76.356	-0.06	0.07
3.500	303.143	78.146	78.166	-0.02	0.03
3.500	323.140	85.324	85.367	-0.05	0.05
3.500	348.143	94.279	94.310	-0.03	0.03
3.500	373.150	103.203	103.198	0.00	-0.00
3.500	398.160	112.073	112.039	0.03	-0.03
4.000	273.150	75.307	75.354	-0.06	0.07
4.000	298.142	85.992	86.049	-0.07	0.07
4.000	303.143	88.142	88.175	-0.04	0.04
4.000	323.140	96.585	96.638	-0.06	0.06
4.000	348.143	107.094	107.143	-0.05	0.05
4.000	373.150	117.577	117.581	-0.00	0.00
4.000	398.160	127.993	127.961	0.02	-0.02
4.500	273.150	83.156	83.208	-0.06	0.07
4.500	298.142	95.511	95.577	-0.07	0.08
4.500	303.143	98.002	98.035	-0.03	0.04

TABLE 4. *Methane densities of Douslin et al. [22]—Continued*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
4.500	323.140	107.779	107.820	−0.04	0.04
4.500	348.143	119.920	119.965	−0.04	0.04
4.500	373.150	132.013	132.030	−0.01	0.01
4.500	398.160	144.083	144.026	0.04	−0.04
5.000	273.150	90.802	90.868	−0.07	0.09
5.000	298.142	104.911	104.986	−0.07	0.08
5.000	303.143	107.745	107.792	−0.04	0.05
5.000	323.140	118.912	118.962	−0.04	0.05
5.000	348.143	132.781	132.827	−0.03	0.04
5.000	373.150	146.583	146.600	−0.01	0.01
5.000	398.160	160.346	160.293	0.03	−0.03
5.500	273.150	98.315	98.381	−0.07	0.08
5.500	298.142	114.261	114.327	−0.06	0.06
5.500	303.143	117.449	117.498	−0.04	0.05
5.500	323.140	130.030	130.119	−0.07	0.07
5.500	348.143	145.748	145.787	−0.03	0.03
5.500	373.150	161.321	161.351	−0.02	0.02
5.500	398.160	176.887	176.827	0.03	−0.03
6.000	273.150	105.680	105.793	−0.11	0.13
6.000	298.142	123.585	123.650	−0.05	0.06
6.000	303.143	127.160	127.202	−0.03	0.04
6.000	323.140	141.261	141.342	−0.06	0.06
6.000	348.143	158.896	158.902	−0.00	0.00
6.000	373.150	176.308	176.348	−0.02	0.02
6.000	398.160	193.701	193.694	0.00	−0.00
6.500	273.150	113.057	113.153	−0.08	0.10
6.500	298.142	132.941	133.007	−0.05	0.05
6.500	303.143	136.921	136.958	−0.03	0.03
6.500	323.140	152.692	152.691	0.00	−0.00
6.500	348.143	172.195	172.234	−0.02	0.02
6.500	373.150	191.585	191.655	−0.04	0.03
6.500	398.160	211.015	210.966	0.02	−0.02
7.000	273.150	120.494	120.510	−0.01	0.02
7.000	298.142	142.411	142.453	−0.03	0.03
7.000	303.143	146.809	146.822	−0.01	0.01
7.000	323.140	164.208	164.225	−0.01	0.01
7.000	348.143	185.865	185.850	0.01	−0.01
7.000	373.150	207.347	207.346	0.00	−0.00
7.000	398.160	228.706	228.722	−0.01	0.01
7.500	273.150	127.854	127.913	−0.05	0.05
7.500	298.142	152.040	152.044	−0.00	0.00
7.500	303.143	156.783	156.851	−0.04	0.04
7.500	323.140	175.966	176.007	−0.02	0.02
7.500	348.143	199.807	199.821	−0.01	0.01
7.500	373.150	223.440	223.497	−0.03	0.02
7.500	398.160	247.053	247.045	0.00	−0.00
8.000	273.150	135.410	135.417	−0.01	0.01
8.000	298.142	161.873	161.844	0.02	−0.02
8.000	303.143	167.135	167.111	0.01	−0.01
8.000	323.140	188.142	188.109	0.02	−0.02
8.000	348.143	214.218	214.222	−0.00	0.00
8.000	373.150	240.078	240.192	−0.05	0.04
8.000	398.160	266.023	266.023	−0.00	0.00
8.500	273.150	143.090	143.080	0.01	−0.01
8.500	298.142	171.979	171.918	0.04	−0.04
8.500	303.143	177.736	177.669	0.04	−0.04
8.500	323.140	200.673	200.604	0.03	−0.03
8.500	348.143	229.193	229.139	0.02	−0.02
8.500	373.150	257.427	257.522	−0.04	0.03

TABLE 4. *Methane densities of Douslin et al. [22]—Continued*

MOL/L	T, K	P, BAR	P, CALC	P, PCT	D, PCT
8.500	398.160	285.758	285.756	0.00	-0.00
9.000	273.150	151.095	150.964	0.09	-0.09
9.000	298.142	182.470	182.341	0.07	-0.07
9.000	303.143	188.733	188.602	0.07	-0.07
9.000	323.140	213.759	213.577	0.09	-0.08
9.000	348.143	244.766	244.660	0.04	-0.04
9.000	373.150	275.434	275.585	-0.05	0.05
9.000	398.160	306.209	306.349	-0.05	0.04
9.500	273.150	159.307	159.142	0.10	-0.10
9.500	298.142	193.423	193.194	0.12	-0.11
9.500	303.143	200.116	199.993	0.06	-0.06
9.500	323.140	227.366	227.118	0.11	-0.09
9.500	348.143	261.024	260.888	0.05	-0.04
9.500	373.150	294.478	294.490	-0.00	0.00
9.500	398.160	327.865	327.918	-0.02	0.01
10.000	273.150	167.979	167.694	0.17	-0.16
10.000	298.142	204.825	204.570	0.12	-0.11
10.000	303.143	212.100	211.935	0.08	-0.07
10.000	323.140	241.534	241.329	0.09	-0.07
10.000	348.143	278.048	277.931	0.04	-0.03
10.000	373.150	314.250	314.355	-0.03	0.03
10.000	398.160	350.494	350.589	-0.03	0.02
10.500	273.150	177.002	176.711	0.16	-0.15
10.500	298.142	216.938	216.570	0.17	-0.14
10.500	303.143	224.805	224.534	0.12	-0.10
10.500	323.140	256.572	256.321	0.10	-0.08
10.500	348.143	296.014	295.912	0.03	-0.03
10.500	373.150	335.101	335.310	-0.06	0.05
10.500	398.160	374.301	374.500	-0.05	0.04
11.000	273.150	186.780	186.294	0.26	-0.22
11.000	298.142	229.688	229.307	0.17	-0.13
11.000	303.143	238.292	237.903	0.16	-0.13
11.000	323.140	272.539	272.219	0.12	-0.09
11.000	348.143	315.031	314.962	0.02	-0.02
11.000	373.150	357.297	357.495	-0.06	0.04
11.000	398.160	399.523	399.798	-0.07	0.05
11.500	273.150	197.051	196.557	0.25	-0.20
11.500	298.142	243.451	242.905	0.22	-0.17
11.500	303.143	252.507	252.170	0.13	-0.10
11.500	323.140	289.542	289.157	0.13	-0.10
11.500	348.143	335.104	335.226	-0.04	0.03
11.500	373.150	380.866	381.064	-0.05	0.04
12.000	273.150	208.211	207.621	0.28	-0.21
12.000	298.142	257.950	257.501	0.17	-0.12
12.000	303.143	267.883	267.472	0.15	-0.11
12.000	323.140	307.555	307.281	0.09	-0.06
12.000	348.143	356.651	356.860	-0.06	0.04
12.000	373.150	405.932	406.182	-0.06	0.04
12.500	273.150	220.275	219.620	0.30	-0.21
12.500	298.142	273.788	273.241	0.20	-0.13
12.500	303.143	284.252	283.960	0.10	-0.07
12.500	323.140	326.974	326.751	0.07	-0.04
12.500	348.143	379.993	380.035	-0.01	0.01

3. The Coexistence Densities

To obtain densities of freezing and of saturated liquid, we represent initial points of each experimental pseudo-isochore from table 1 by

$$P = A + B \cdot T + C/T + D/T^2, \quad (1)$$

used for extrapolation to the $P(T)$ melting- and vapor-pressure lines of [7] respectively. Adjustment is made for the negligible change of density over the range of extrapolation. On the melting line, we obtain three densities to a maximum pressure of 220 bar. On the vapor pressure line, we obtain 19 densities to a maximum temperature of 175 K. Vapor densities are obtained by use of the virial equation of [5] and vapor pressures of [7] to a maximum temperature of 175 K.

The analytical functions used to represent these densities are given in the appendix. The single-valued function $T_s(\rho)$ for coexisting vapor and liquid then was adjusted to data from the above functions. We omit details of all this tedious work because they are not essential to development of the equation of state. They will be given in later reports. For the saturated liquid, however, we give in Appendix table 1 the derived and calculated densities because these are of especial technological importance.

4. The Equation of State

On the notorious problem of the equation of state [14, 14a], we have investigated further a form which is nonanalytic at the critical point [15], rectifying one defect and making simplifications. For background, it was found with hydrogen that an excellent isochoric equation is of the form

$$(Z-1) \cdot x/\rho = A + B \cdot T + C/T + D/T^2, \quad (2)$$

provided we avoid the neighborhood of saturation and that we modify the second term on the right for consistency with high-temperature behavior of the second virial coefficient. We then modified the last term on the right to obtain $C_v \rightarrow \infty$ on approach to the critical point, as computed along the critical isotherm by means of the thermodynamic relation

$$C_v(\rho, T) = C_v^0(T) - T \cdot \int_0^\rho (\partial^2 P / \partial T^2)_\rho d\rho / \rho^2. \quad (3)$$

We now have developed the following isochoric equation of state for methane via many exploratory computations

$$(Z-1) \cdot x/\rho = A + B \cdot \Phi(T) + C/x + D \cdot \Psi(\rho, T). \quad (4)$$

The temperature-dependent functions are

$$\Phi(T) \equiv x \cdot [1 - \exp(-b - \beta/x)], \quad (4a)$$

$$\Psi(\rho, T) \equiv [1 - \omega \cdot \ln(1 + 1/\omega)]/x. \quad (4b)$$

The argument ω is defined

$$\omega(\rho, T) \equiv (T - \theta)/(\delta \cdot T_c) \quad (4c)$$

by use of the locus of temperatures

$$\theta(\rho) \equiv T_s(\rho) \cdot \exp[-u(\sigma)/2], \quad (4d)$$

where $u(\sigma)$ is defined

$$u(\sigma) \equiv \alpha_g \cdot [|\sigma - 1|^3 - (\sigma - 1)^3] + \alpha_l \cdot [|\sigma - 1|^3 + (\sigma - 1)^3].$$

The saturation temperatures $T_s(\rho)$ are given in the appendix.

Density-dependent coefficients of (4) are formulated as power series,

$$A(\rho) \equiv \sum_{i=0}^3 A_i \cdot \rho^i, \quad B(\rho) \equiv \sum_{i=0}^2 B_i \cdot \rho^i,$$

$$C(\rho) \equiv \sum_{i=1}^3 C_i \cdot \rho^i, \quad D(\rho) \equiv (\sigma - 1) \cdot \sum_{i=0}^2 D_i \cdot \rho^i.$$

An essential modification from [15] is the above formulation of $\theta(\rho)$. The quadratic $(\sigma - 1)^2$, formerly used in the exponential, gives a logarithmic infinity in $\partial^3 P / \partial \rho^3$ at the critical point.

Coefficients of (4) are found by least squares after multiplying each polynomial throughout by its temperature-dependent factor. Via the least squares program [16], we impose four constraints: the pressure shall be our assigned values at the triple- and critical-points; and we shall have $\partial P / \partial \rho = \partial^2 P / \partial \rho^2 = 0$ at the critical point.

Experimental PVT data from four sources cover virtually the entire domain of interest here, namely $T_t < T < 400$ K and $P \leq 350$ bar. Table 5 gives these sources and the range of their data in T , P , and d . We then give the number of data, N , selected for present work. The last two columns give the mean of relative pressure deviations $\Delta P/P$ and the rms of relative density deviations $\Delta d/d$, each from eq (4) with constants given below.

The constants of eq (4) for methane are given in the last column of table 6. Behavior of the coefficients $A(\rho) \dots D(\rho)$ is quite similar to plots given in [15]. A calculated table of P and of $\partial P / \partial \rho$ along the critical isotherm shows that $\partial P / \partial \rho = 0$ at the critical point, and $\partial P / \partial \rho > 0$ at all adjacent densities. Higher derivatives through $\partial^4 P / \partial \rho^4$ also should be zero at the critical point according to a recent scaling-law equation of state [17], but we have not investigated these for eq (4).

Complete PVT data and deviations are given by tables 1 through 4 in response to readers' requests. The source of data is given by the heading for each table. Columns give the density in mol/l, the temperature, the pressure, the calculated pressure, and, in the last two columns, the relative deviations of pres-

TABLE 5. Data used for the equation of state

Source	Range of the data				Δ , %	
	T , K	P , bar	d , mol/l	N	P	d
Virial eq [5].....	140-270	5-46	0.5-2.0	96	0.05	0.09
Vennix [13].....	172-273	25-400	2.5-17.5	133	0.22	0.26
This report.....	94-245	20-350	18-28.5	279	0.66	0.03
Douslin [22].....	273-398	16-400	0.75-12.5	171	0.05	0.06

sure and of density from eq (4), respectively, expressed in percent.

The reader should note that the derivative $(\partial P/\partial \rho)_T$ approaches zero at the critical point. Density deviations in this region (Vennix data) therefore should be ignored. This derivative becomes extremely large, on the other hand, for compressed liquid at low temperatures, and here the pressure deviations (NBS data) should be ignored.

5. Comments on the Equation of State

Equation (4) yields the perfect gas law $Z=1$ in the limit of low density. In the limit of high temperature it approximates the perfect gas, and yields $Z=1$ for the special case $b=0$. Due to its structure and relatively small number of least-squares coefficients, it tends to preserve important qualitative characteristics of the $P(\rho, T)$ surface. Among these are consistency with the known behavior of some specific heats [18]. For methane, we have examined the shape of isochores from eq (4), finding that they have monotonically negative curvature, $\partial^2 P/\partial T^2$, at $\rho < \rho_c$; a sigmoid shape in the range $1 < \rho/\rho_c < 2$; and (unlike hydrogen) negative curvature again at higher densities. The critical isochore has a very small, positive curva-

ture at the critical point, similar to results for hydrogen [15].

The nonanalytic function $\Psi(\rho, T)$, eq (4b), is designed to give a large increase of C_v upon close approach to the critical point. It is similar to that used for hydrogen [15], through transformation of variables. Via the definition (4c) for $\omega(\rho, T)$, however, we now have the fact that $\Psi(\rho, T)$ exists in the limit $\theta \rightarrow 0$, whereas formerly it vanished. This function Ψ behaves like $1/T^2$ at high temperatures. At low temperatures, it terminates with a value of $1/x$ on the locus of temperatures $\theta(\rho)$ inside the coexistence envelope, at which point it gives infinite curvature $\partial^2 P/\partial T^2$. As density increases through the critical point, the sign of this curvature is reversed by means of the root $(\sigma - 1)$ in the formula for coefficient $D(\rho)$.

Temperature dependence in eq (4) is similar to that of the well-known Beattie-Bridgeman equation,

$$(Z - 1) \cdot x/\rho = \bar{A} + \bar{B} \cdot x + \bar{D}/x^2, \quad (5)$$

in domains away from saturation. In particular, the absence of a constant term in our formula for $C(\rho)$ means that a term in $1/T^2$ is missing from description of the second virial coefficient, consistent with (5).

We have used eq (4) for extrapolation at pressures up to 700 bar (10,000 psi) along isochores at $T \leq 400$ K, finding that the pressure increases monotonically and that the derivatives $\partial P/\partial T$ and $\partial P/\partial \rho$ are well-behaved. This is noteworthy for the compressed liquid at low temperatures because few if any of the well-known equations of state can pass this test and at the same time represent PVT data over the enormous range of the entire $P(\rho, T)$ surface, from ideal gas states up to compressed liquid states near the melting line at low temperatures.

The number of temperature-dependent terms in equation (4) appears to exceed the number needed for qualitative description of isochores. The second term on the right gives weak negative curvature at high temperatures, and the last term may give curvature of either sign at low temperatures. We have, indeed, formulated an equation like eq (4) for methane, omitting the term $C(\rho)/x$ [19]. This was prior to our PVT measurements on the compressed liquid. As with hydrogen, we have found a term in $1/x$ necessary on the right of eq (4) to obtain a reasonably precise representation of PVT data when these include the compressed liquid states.

We have applied the present equation of state to hydrogen and to oxygen without any special difficulties, indicating therefore that it is not unique for

TABLE 6. Constants of equation (4) for H₂, O₂, and CH₄

Constant	Hydrogen	Oxygen	Methane
T_t , K	13.800	54.3507	90.680
T_c , K	32.962	154.52	190.53
d_t , mol/l	38.203	40.83	28.1472
d_c , mol/l	15.59	13.52	10.15
P_t , *	0.0695	0.0015	0.1174
P_c , *	12.704	49.650	45.957
α_g	0.3	0.4	0.5
α_1	.1	.4	.5
b	.8	1	.8
β	7	3	4
δ	1	1	1.2
A_0	-3.6990 3501	-4.7457 9188	-4.1545 2847
A_1	-1.5630 8113	-3.6883 8499	-4.7739 0186
A_2	5.0231 6164	-1.1695 4201	3.5199 9044
A_3	-0.7443 2571	8.2956 4587	4.2573 7412
B_0	1.2426 3871	2.0447 2804	1.7474 4656
B_1	0.6032 6565	2.5732 0035	2.5767 9569
B_2	.0692 4977	2.1530 4750	0.4653 8980
C_1	3.9354 2987	5.3321 8510	5.1033 5931
C_2	-9.9450 4679	-13.4213 9863	-12.4202 2748
C_3	5.7268 9781	7.6933 8807	6.3612 4273
D_0	1.0188 2911	1.7942 7732	1.8838 3919
D_1	-2.1414 4245	-3.1707 7491	-3.5471 3477
D_2	1.2924 7888	1.2788 3788	1.8740 8815

*For H₂ and O₂ the equation of state is in atmospheres; for CH₄, in bars.

methane. Densities for these other gases also ranged up to the melting line. Saturation temperatures $T_s(\rho)$ are given in [21]. In some cases the coefficients A_3 and B_2 for eq (4) show a low significance, suggesting that the corresponding terms of eq (4) might be omitted when PVT data extend to densities no higher than about $2 \cdot \rho_c$. In table 6 we see that coefficients for all three substances are similar and mostly of the same sign.

The authors are indebted to R. D. McCarty for use of the least squares program open to constraints [16], and to D. E. Diller and L. A. Weber for many discussions and important suggestions.

6. Appendix

6.1. Functions for Densities on the Coexistence Boundaries

(1) The freezing liquid densities are described by

$$d/d_t = (T/T_t)^{1/4},$$

a form developed for hydrogen [20].

(2) The saturated liquid densities are described as in [6] by

$$\bar{d}_l/d_c = 1 + a \cdot z + b \cdot z^{0.36} + c \cdot \exp[-\epsilon \cdot x^2/z],$$

where $x \equiv T/T_c$, $z \equiv (1-x)$, and

$$\begin{aligned} a &= 0.539\,403 & c &= -0.018\,387, \\ b &= 1.896\,635 & \epsilon &= 0.88. \end{aligned}$$

The triple point liquid density from this equation is $d_t = 28.1472$ mol/l. Derived and calculated values are given in Appendix table 1 below.

TABLE A1. *Derived and calculated densities of saturated liquid methane*

T, K	Mol/l	Calculated	Percent
175.053	18.390	18.392	-0.01
169.326	19.492	19.492	0.00
163.699	20.428	20.425	0.02
157.199	21.379	21.379	-0.00
151.555	22.130	22.131	-0.00
145.448	22.880	22.882	-0.01
139.352	23.578	23.581	-0.01
133.773	24.186	24.186	0.00
133.878	24.176	24.175	0.01
129.657	24.611	24.613	-0.01
125.825	24.999	24.999	0.00
121.893	25.388	25.383	0.02
117.746	25.782	25.778	0.01
113.772	26.146	26.147	-0.00
109.611	26.527	26.525	0.01
105.165	26.916	26.919	-0.01
101.434	27.243	27.243	0.00
97.173	27.605	27.606	-0.01
93.512	27.910	27.913	-0.01

(3) The saturated vapor densities are described more simply than in [6] by

$$\ln(d_g/d_c) = A_1 \cdot w + A_2 \cdot w^{1/3} + \sum_{i=3}^5 A_i \cdot w^{i-2},$$

where

$$u \equiv (T_c - T)/(T_c - T_t), \quad w \equiv (T_c/T - 1)/(T_c/T_t - 1),$$

$$A_1 = -6.815\,239, \quad A_4 = 0.736\,090,$$

$$A_2 = -2.012\,860, \quad A_5 = 0.416\,449.$$

$$A_3 = 1.203\,942,$$

(4) The saturation temperature $T_s(\rho)$ for coexisting vapor and liquid are described here by a function which is constrained to the triple point, in contrast with our earlier form [21]. Define the variables.

$$Y(T_s) \equiv (T_c/T_s - 1)/(T_c/T_t - 1),$$

$$U(\rho) \equiv (\sigma - 1)/(\sigma_t - 1),$$

$$F(\rho) \equiv \sum_{i=2}^8 A_i \cdot \rho^{i-2},$$

where σ_t is the constant, d_t/d_c . The function now is

$$Y(T_s) = U^{3/8} \cdot [1 + A_1 \cdot \ln(\rho) + (\rho - 1) \cdot F(\rho)],$$

$$A_1 = -0.814\,6680, \quad A_5 = -142.308\,6536,$$

$$A_2 = 2.482\,4192, \quad A_6 = 240.076\,9868,$$

$$A_3 = -6.872\,7440, \quad A_7 = -195.876\,1459,$$

$$A_4 = 43.037\,4662, \quad A_8 = 63.300\,1385.$$

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