Refractive Index and Density Isotherms for Methane from 273 to 373 K and at Pressures up to 34 MPa

Hans J. Achtermann* **and Jianguo Hong**

Institut für Thermodynamik, Universität Hannover, D-3000 Hannover, Germany

Wolfgang Wagner and Andreas Pruss

Institut für Thermo- und Fluiddynamik, Ruhr-Universität Bochum, D-4630 Bochum, Germany

Comprehensive refractive index measurements $n(P,T)$ were carried out on pure methane in the temperature range from 273.15 to 373.15 K and at pressures up to 34 MPa. Two coupled laser interferometers were used for the experiments, one containing methane, the other the reference gas nitrogen maintained at the same pressure and a fixed temperature T_0, serving as a manometer. The uncertainty of the refractive index was estimated to be less than $\pm 5 \times 10^{-7}$ at 1 MPa and $\pm 5 \times 10^{-6}$ at 34 MPa. To measure the higher-order refractivity virial coefficients B_R, C_R, ... of the Lorentz–Lorenz expansion, overflow experiments were made on the 323.15 K isotherm at pressures up to 35 MPa. In the investigated range of pressure B_R and C_R are the only significant refractivity virial coefficients. A comparison with literature values shows that B_R and C_R are independent of temperature in the range from 220 to 373 K. On the basis of $n(P,T)$ measurements, the density $\rho(P,T)$ was calculated by including B_R and C_R. The uncertainty of the density was estimated to be not greater than ±0.05%.

Introduction

The importance of the refractive index measured in a wide range of pressures and temperatures is increasing, since absolute and differential measurements of the refractive index can be used to determine accurate values of the density (*1–3*). The refractive index data can also be used to discriminate between the various equations of state of a pure fluid and as a local probe of properties, such as the density, that cannot readily be measured in situ (*4*).

This paper presents comprehensive (pressure P, refractive index n, and temperature T) measurements on pure methane along six isotherms in the temperature range from 273.15 to 373.15 K at pressures up to 34 MPa. The higher-order refractivity virial coefficients B_R, C_R, ... of the Lorentz–Lorenz expansion were measured independently by making overflow experiments on the 323.15 K isotherm at pressures up to 35 MPa. In the investigated range of pressure, B_R and C_R are the only significant refractivity virial coefficients for methane. Our results together with literature values show that B_R and C_R are independent of temperature in the range from 220 to 373 K.

Accurate knowledge of the refractivity virial coefficients offers a potentially useful method of density determination through refractive index measurements. On the basis of the 654 experimental $n(P,T)$ data including the coefficients B_R and C_R, we calculated accurate values of density $\rho(P,T)$ by solving directly the Lorentz–Lorentz (LL) expansion

$$\mathrm{LL} = \frac{n^2 - 1}{n^2 + 2}\rho^{-1} = A_R + B_R\rho + C_R\rho^2 + ... \qquad (1)$$

In general, for density calculations up to twice the critical density the LL expansion can be truncated after the third term, and in some cases, such as for C_2H_4, C_2H_6, and SF_6, after the fourth term. This is due to the fact that the LL expansion has a simpler dependence on density than the refractive index itself. The density data of this work have been compared with selected measurements of other researchers using the new equation of state for methane recently developed by Setzmann and Wagner (*5*) which covers the range from the melting line to 625 K at pressures up to 1000 MPa.

Experimental Section

Refractive Index Measurements. The experimental details for measuring the absolute refractive index as a function of pressure and temperature have been described in detail previously (*1, 2*). The optical apparatus essentially consists of two coupled laser interferometers. One interferometer measures the refractive index of the sample, while the second interferometer, maintained at the same pressure, is used to determine the pressure simultaneously by measuring the refractive index of nitrogen at a fixed temperature T_0. The relation between the refractive index of nitrogen and the pressure was previously established for the 323.15 K isotherm by comparing the fringe count K_P of the interferometer filled with nitrogen with the pressure P measured with a precision piston gauge. In this way the relation $P = P(K_P,T_0)$ is given (*6*). A differential pressure indicator is only used for the filling and coupling procedure of the two interferometers. During the expansion run, the valve between the interferometers is open and the pressure can be automatically equalized by means of a pressure equilibrium chamber between the two interferometers. This ensures the possibility of obtaining the variables n and P simultaneously. The small volume of the gases in the interferometers (3 mm in diameter and with lengths between 47 and 250 mm) renders the measurements extremely fast. The achievement of the isothermal conditions between two measurement points takes only 1–5 min.

Determination of the Higher-Order Refractivity Virial Coefficients. The method, apparatus, and procedure for the experimental determination of the higher-order refractivity virial coefficients B_R, C_R, ... have been described in detail previously (*3*). The direct determination of B_R, C_R, ... is based on isothermal measurements of the excess

* To whom correspondence should be addressed.

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Table I. Experimental Refractive Indices n of Methane and Calculated Densities ρ from the Refractive Index Values by Including the Refractivity Virial Coefficients A_R, B_R, and C_R

	273.15 K		283.15 K		293.15 K		323.15 K		348.15 K		373.15 K	
P/MPa	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)
1.00	1.004 450	0.4509	1.004 282	0.4337	1.004 126	0.4179	1.003 721	0.3769	1.003 444	0.3487	1.003 203	0.3244
1.10	1.004 908	0.4972	1.004 721	0.4782	1.004 548	0.4606	1.004 099	0.4151	1.003 792	0.3839	1.003 526	0.3571
1.20	1.005 368	0.5437	1.005 161	0.5227	1.004 971	0.5034	1.004 479	0.4535	1.004 141	0.4192	1.003 849	0.3898
1.30	1.005 829	0.5904	1.005 604	0.5675	1.005 395	0.5463	1.004 858	0.4919	1.004 490	0.4545	1.004 173	0.4225
1.40	1.006 294	0.6374	1.006 048	0.6124	1.005 822	0.5894	1.005 239	0.5304	1.004 840	0.4899	1.004 497	0.4553
1.50	1.006 761	0.6846	1.006 496	0.6576	1.006 250	0.6327	1.005 621	0.5690	1.005 191	0.5254	1.004 822	0.4882
1.60	1.007 230	0.7320	1.006 944	0.7029	1.006 680	0.6762	1.006 003	0.6076	1.005 542	0.5609	1.005 147	0.5210
1.70	1.007 703	0.7798	1.007 394	0.7484	1.007 112	0.7198	1.006 387	0.6464	1.005 895	0.5965	1.005 473	0.5540
1.80	1.008 176	0.8276	1.007 848	0.7942	1.007 545	0.7635	1.006 772	0.6853	1.006 247	0.6321	1.005 799	0.5869
1.90	1.008 652	0.8757	1.008 302	0.8401	1.007 979	0.8074	1.007 158	0.7243	1.006 600	0.6678	1.006 126	0.6200
2.00	1.009 131	0.9240	1.008 759	0.8862	1.008 416	0.8515	1.007 544	0.7633	1.006 955	0.7036	1.006 453	0.6530
2.10	1.009 613	0.9727	1.009 217	0.9325	1.008 855	0.8958	1.007 932	0.8025	1.007 309	0.7394	1.006 780	0.6860
2.20	1.010 096	1.0214	1.009 678	0.9790	1.009 295	0.9402	1.008 321	0.8417	1.007 665	0.7753	1.007 108	0.7192
2.30	1.010 583	1.0706	1.010 141	1.0257	1.009 736	0.9847	1.008 711	0.8811	1.008 022	0.8113	1.007 436	0.7523
2.40	1.011 071	1.1198	1.010 606	1.0726	1.010 179	1.0294	1.009 101	0.9205	1.008 379	0.8474	1.007 765	0.7855
2.50	1.011 563	1.1694	1.011 072	1.1196	1.010 624	1.0743	1.009 494	0.9601	1.008 736	0.8834	1.008 093	0.8186
2.60	1.012 057	1.2192	1.011 541	1.1669	1.011 071	1.1194	1.009 886	0.9997	1.009 094	0.9195	1.008 424	0.8520
2.70	1.012 554	1.2693	1.012 012	1.2144	1.011 520	1.1646	1.010 280	1.0394	1.009 453	0.9557	1.008 754	0.8853
2.80	1.013 053	1.3196	1.012 486	1.2621	1.011 970	1.2100	1.010 675	1.0792	1.009 813	0.9920	1.009 085	0.9187
2.90	1.013 555	1.3702	1.012 961	1.3100	1.012 422	1.2555	1.011 071	1.1192	1.010 173	1.0283	1.009 416	0.9521
3.00	1.014 060	1.4211	1.013 439	1.3582	1.012 875	1.3012	1.011 468	1.1592	1.010 534	1.0647	1.009 747	0.9855
3.10	1.014 567	1.4721	1.013 918	1.4064	1.013 331	1.3471	1.011 866	1.1993	1.010 895	1.1011	1.010 079	1.0190
3.20	1.015 076	1.5234	1.014 400	1.4549	1.013 789	1.3932	1.012 264	1.2394	1.011 257	1.1376	1.010 409	1.0523
3.30	1.015 589	1.5750	1.014 884	1.5036	1.014 248	1.4394	1.012 664	1.2797	1.011 620	1.1742	1.010 742	1.0859
3.40	1.016 104	1.6268	1.015 370	1.5526	1.014 708	1.4857	1.013 065	1.3201	1.011 983	1.2107	1.011 075	1.1194
3.50	1.016 622	1.6789	1.015 858	1.6017	1.015 171	1.5323	1.013 467	1.3605	1.012 347	1.2474	1.011 409	1.1531
3.60	1.017 142	1.7312	1.016 348	1.6509	1.015 635	1.5790	1.013 869	1.4010	1.012 711	1.2841	1.011 742	1.1866
3.70	1.017 666	1.7839	1.016 841	1.7005	1.016 100	1.6258	1.014 273	1.4417	1.013 076	1.3208	1.012 076	1.2203
3.80	1.018 191	1.8367	1.017 335	1.7502	1.016 568	1.6728	1.014 677	1.4823	1.013 442	1.3577	1.012 410	1.2539
3.90	1.018 720	1.8899	1.017 833	1.8002	1.017 037	1.7200	1.015 083	1.5232	1.013 808	1.3945	1.012 745	1.2877
4.00	1.019 252	1.9433	1.018 333	1.8505	1.017 509	1.7674	1.015 489	1.5640	1.014 175	1.4314	1.013 080	1.3214
4.10	1.019 785	1.9968	1.018 833	1.9007	1.017 982	1.8150	1.015 897	1.6051	1.014 543	1.4685	1.013 416	1.3552
4.20	1.020 323	2.0509	1.019 336	1.9512	1.018 456	1.8626	1.016 305	1.6461	1.014 911	1.5055	1.013 752	1.3891
4.30	1.020 865	2.1053	1.019 842	2.0020	1.018 933	1.9105	1.016 714	1.6872	1.015 279	1.5425	1.014 088	1.4229
4.40	1.021 408	2.1598	1.020 350	2.0530	1.019 412	1.9586	1.017 125	1.7285	1.015 649	1.5797	1.014 425	1.4568
4.50	1.021 953	2.2145	1.020 860	2.1042	1.019 892	2.0068	1.017 536	1.7698	1.016 019	1.6169	1.014 763	1.4908
4.60	1.022 502	2.2695	1.021 372	2.1556	1.020 374	2.0552	1.017 948	1.8112	1.016 389	1.6541	1.015 099	1.5246
4.70	1.023 052	2.3247	1.021 887	2.2073	1.020 856	2.1035	1.018 362	1.8528	1.016 760	1.6914	1.015 436	1.5585
4.80	1.023 606	2.3802	1.022 403	2.2590	1.021 342	2.1523	1.018 775	1.8943	1.017 131	1.7287	1.015 774	1.5925
4.90	1.024 163	2.4361	1.022 923	2.3112	1.021 829	2.2012	1.019 190	1.9360	1.017 503	1.7660	1.016 113	1.6266
5.00	1.024 722	2.4921	1.023 444	2.3634	1.022 316	2.2500	1.019 606	1.9777	1.017 876	1.8035	1.016 452	1.6607
5.25	1.026 134	2.6335	1.024 754	2.4946	1.023 546	2.3733	1.020 649	2.0824	1.018 811	1.8974	1.017 300	1.7459
5.50	1.027 563	2.7765	1.026 081	2.6275	1.024 787	2.4976	1.021 699	2.1877	1.019 747	1.9913	1.018 150	1.8313
5.75	1.029 010	2.9213	1.027 421	2.7616	1.026 038	2.6229	1.022 753	2.2934	1.020 688	2.0857	1.019 002	1.9168
6.00	1.030 474	3.0676	1.028 774	2.8969	1.027 299	2.7490	1.023 813	2.3996	1.021 631	2.1803	1.019 856	2.0026
6.25	1.031 957	3.2158	1.030 141	3.0336	1.028 571	2.8762	1.024 877	2.5062	1.022 578	2.2752	1.020 711	2.0884
6.50	1.033 457	3.3655	1.031 521	3.1714	1.029 853	3.0044	1.025 948	2.6134	1.023 528	2.3704	1.021 569	2.1744
6.75	1.034 975	3.5169	1.032 914	3.3104	1.031 145	3.1334	1.027 023	2.7209	1.024 481	2.4658	1.022 428	2.2605
7.00	1.036 509	3.6698	1.034 320	3.4507	1.032 447	3.2634	1.028 104	2.8290	1.025 436	2.5614	1.023 288	2.3467
7.25	1.038 061	3.8244	1.035 739	3.5921	1.033 759	3.3943	1.029 188	2.9374	1.026 393	2.6572	1.024 150	2.4331
7.50	1.039 630	3.9806	1.037 170	3.7347	1.035 080	3.5260	1.030 279	3.0464	1.027 354	2.7533	1.025 014	2.5196
7.75	1.041 214	4.1381	1.038 613	3.8784	1.036 410	3.6585	1.031 372	3.1555	1.028 317	2.8496	1.025 879	2.6062
8.00	1.042 814	4.2972	1.040 068	4.0231	1.037 749	3.7918	1.032 470	3.2651	1.029 282	2.9460	1.026 745	2.6928
8.25	1.044 429	4.4576	1.041 532	4.1687	1.039 096	3.9259	1.033 572	3.3750	1.030 249	3.0426	1.027 612	2.7795
8.50	1.046 058	4.6193	1.043 010	4.3155	1.040 452	4.0608	1.034 677	3.4852	1.031 218	3.1393	1.028 480	2.8663
8.75	1.047 703	4.7824	1.044 496	4.4631	1.041 815	4.1962	1.035 786	3.5957	1.032 190	3.2363	1.029 349	2.9531
9.00	1.049 359	4.9465	1.045 993	4.6116	1.043 186	4.3324	1.036 899	3.7065	1.033 163	3.3333	1.030 219	3.0400
9.25	1.051 027	5.1117	1.047 499	4.7610	1.044 564	4.4692	1.038 014	3.8175	1.034 137	3.4304	1.031 089	3.1269
9.50	1.052 708	5.2781	1.049 012	4.9109	1.045 948	4.6065	1.039 132	3.9288	1.035 113	3.5277	1.031 961	3.2139
9.75	1.054 399	5.4453	1.050 534	5.0616	1.047 337	4.7443	1.040 253	4.0402	1.036 090	3.6250	1.032 833	3.3009
10.00	1.056 099	5.6133	1.052 063	5.2129	1.048 733	4.8826	1.041 377	4.1520	1.037 069	3.7224	1.033 705	3.3879
10.50	1.059 519	5.9509	1.055 139	5.5171	1.051 538	5.1603	1.043 630	4.3757	1.039 029	3.9174	1.035 451	3.5619
11.00	1.062 964	6.2905	1.058 234	5.8227	1.054 359	5.4392	1.045 893	4.6002	1.040 992	4.1126	1.037 198	3.7359
11.50	1.066 418	6.6305	1.061 340	6.1289	1.057 188	5.7186	1.048 155	4.8245	1.042 956	4.3076	1.038 944	3.9096
12.00	1.069 872	6.9700	1.064 450	6.4352	1.060 022	5.9982	1.050 422	5.0489	1.044 921	4.5026	1.040 689	4.0831
12.50	1.073 315	7.3080	1.067 557	6.7408	1.062 858	6.2776	1.052 690	5.2733	1.046 885	4.6973	1.042 433	4.2563
13.00	1.076 733	7.6430	1.070 652	7.0448	1.065 685	6.5558	1.054 955	5.4971	1.048 847	4.8917	1.044 174	4.4292
13.50	1.080 117	7.9743	1.073 729	7.3467	1.068 502	6.8327	1.057 216	5.7204	1.050 805	5.0855	1.045 912	4.6016
14.00	1.083 458	8.3009	1.076 779	7.6456	1.071 303	7.1077	1.059 471	5.9428	1.052 760	5.2788	1.047 648	4.7736
14.50	1.086 742	8.6216	1.079 795	7.9407	1.074 086	7.3807	1.061 717	6.1641	1.054 707	5.4711	1.049 374	4.9446
15.00	1.089 964	8.9358	1.082 773	8.2319	1.076 837	7.6502	1.063 953	6.3843	1.056 648	5.6628	1.051 096	5.1150
15.50	1.093 117	9.2429	1.085 701	8.5178	1.079 555	7.9162	1.066 176	6.6029	1.058 580	5.8533	1.052 813	5.2848
16.00	1.096 194	9.5423	1.088 582	8.7988	1.082 240	8.1787	1.068 381	6.8196	1.060 502	6.0428	1.054 521	5.4536

Table I. (Continued)

	273.15 K		283.15 K		293.15 K		323.15 K		348.15 K		373.15 K	
P/MPa	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)	n	ρ/(kmol/m^3)
16.50	1.099 188	9.8333	1.091 406	9.0740	1.084 893	8.4378	1.070 569	7.0344	1.062 412	6.2309	1.056 222	5.6216
17.00	1.102 107	10.1167	1.094 171	9.3431	1.087 489	8.6910	1.072 741	7.2475	1.064 312	6.4178	1.057 915	5.7886
17.50	1.104 932	10.3907	1.096 874	9.6059	1.090 048	8.9405	1.074 891	7.4582	1.066 198	6.6033	1.059 597	5.9545
18.00	1.107 674	10.6564	1.099 512	9.8622	1.092 560	9.1851	1.077 019	7.6666	1.068 070	6.7872	1.061 271	6.1194
18.50	1.110 333	10.9138	1.102 086	10.1120	1.095 021	9.4245	1.079 122	7.8724	1.069 927	6.9695	1.062 935	6.2833
19.00	1.112 904	11.1624	1.104 593	10.3551	1.097 431	9.6588	1.081 201	8.0757	1.071 767	7.1500	1.064 587	6.4459
19.50	1.115 396	11.4033	1.107 035	10.5917	1.099 792	9.8880	1.083 255	8.2763	1.073 595	7.3292	1.066 225	6.6069
20.00	1.117 805	11.6359	1.109 411	10.8218	1.102 098	10.1118	1.085 281	8.4741	1.075 403	7.5063	1.067 852	6.7668
20.50	1.120 138	11.8610	1.111 720	11.0451	1.104 353	10.3305	1.087 278	8.6689	1.077 192	7.6815	1.069 467	6.9254
21.00	1.122 393	12.0784	1.113 965	11.2621	1.106 549	10.5432	1.089 246	8.8607	1.078 962	7.8546	1.071 065	7.0822
21.50	1.124 574	12.2885	1.116 147	11.4728	1.108 695	10.7510	1.091 184	9.0495	1.080 711	8.0256	1.072 653	7.2380
22.00	1.126 681	12.4914	1.118 268	11.6776	1.110 790	10.9537	1.093 092	9.2352	1.082 443	8.1948	1.074 225	7.3921
22.50	1.128 721	12.6877	1.120 328	11.8762	1.112 834	11.1513	1.094 971	9.4179	1.084 153	8.3617	1.075 783	7.5447
23.00	1.130 698	12.8778	1.122 330	12.0692	1.114 826	11.3437	1.096 817	9.5973	1.085 845	8.5268	1.077 320	7.6952
23.50	1.132 612	13.0618	1.124 273	12.2564	1.116 768	11.5312	1.098 633	9.7737	1.087 514	8.6895	1.078 854	7.8452
24.00	1.134 464	13.2396	1.126 164	12.4384	1.118 663	11.7141	1.100 418	9.9470	1.089 163	8.8502	1.080 368	7.9933
24.50	1.136 261	13.4122	1.128 000	12.6151	1.120 509	11.8921	1.102 172	10.1172	1.090 790	9.0086	1.081 865	8.1396
25.00	1.138 004	13.5794	1.129 788	12.7870	1.122 313	12.0659	1.103 896	10.2843	1.092 394	9.1647	1.083 348	8.2844
25.50	1.139 692	13.7413	1.131 524	12.9539	1.124 067	12.2349	1.105 590	10.4484	1.093 975	9.3185	1.084 811	8.4272
26.00	1.141 334	13.8987	1.133 214	13.1162	1.125 781	12.3999	1.107 253	10.6095	1.095 538	9.4705	1.086 260	8.5686
26.50	1.142 928	14.0514	1.134 859	13.2741	1.127 450	12.5605	1.108 886	10.7675	1.097 079	9.6202	1.087 693	8.7083
27.00	1.144 478	14.1998	1.136 460	13.4278	1.129 081	12.7173	1.110 490	10.9227	1.098 600	9.7679	1.089 111	8.8465
27.50	1.145 983	14.3439	1.138 019	13.5773	1.130 675	12.8705	1.112 064	11.0748	1.100 091	9.9126	1.090 511	8.9828
28.00	1.147 447	14.4840	1.139 539	13.7230	1.132 224	13.0193	1.113 610	11.2242	1.101 570	10.0560	1.091 895	9.1176
28.50	1.148 873	14.6204	1.141 018	13.8648	1.133 744	13.1653	1.115 127	11.3707	1.103 023	10.1969	1.093 262	9.2506
29.00	1.150 261	14.7531	1.142 462	14.0031	1.135 224	13.3073	1.116 618	11.5146	1.104 457	10.3358	1.094 616	9.3823
29.50	1.151 613	14.8823	1.143 872	14.1381	1.136 670	13.4461	1.118 081	11.6558	1.105 867	10.4724	1.095 950	9.5119
30.00	1.152 933	15.0084	1.145 246	14.2696	1.138 085	13.5818	1.119 518	11.7944	1.107 260	10.6073	1.097 270	9.6402
30.50	1.154 219	15.1312	1.146 589	14.3981	1.139 466	13.7142	1.120 928	11.9303	1.108 630	10.7398	1.098 578	9.7672
31.00	1.155 474	15.2510	1.147 900	14.5235	1.140 817	13.8436	1.122 313	12.0637	1.109 981	10.8705	1.099 867	9.8923
31.50	1.156 699	15.3680	1.149 181	14.6460	1.142 139	13.9702	1.123 672	12.1946	1.111 312	10.9991	1.101 139	10.0157
32.00	1.157 896	15.4822	1.150 430	14.7654	1.143 430	14.0939	1.125 008	12.3232	1.112 619	11.1254	1.102 392	10.1373
32.50	1.159 066	15.5938	1.151 654	14.8823	1.144 697	14.2151	1.126 320	12.4495	1.113 914	11.2505	1.103 635	10.2578
33.00	1.160 210	15.7029	1.152 853	14.9969	1.145 933	14.3334	1.127 609	12.5734	1.115 185	11.3732	1.104 861	10.3766
33.50	1.161 328	15.8094	1.154 023	15.1086	1.147 146	14.4494	1.128 873	12.6950	1.116 433	11.4936	1.106 074	10.4940
34.00	1.162 421	15.9136	1.155 171	15.2182	1.148 333	14.5629	1.130 118	12.8146	1.117 669	11.6129	1.107 269	10.6097

contribution of the Lorentz–Lorenz expansion as a function of density by means of overflow experiments. The measurements are carried out by using the same coupled interferometers as for the $n(P,T)$ measurements, but different cells are used for the experiments. Each interferometer has two similar cells. In the main interferometer the cells are in series and the measuring beam traverses both cells. In the second interferometer the cells are in parallel, where the measuring beam traverses only one cell and the reference beam the other. At the beginning of the overflow experiment one cell in each interferometer is filled with the sample at density ρ_1 and the other is evacuated. Then, by opening the expansion valve between the filled and evacuated cells, the sample is shared with the previously evacuated cells, and at the end of the expansion procedure the initial density is halved ($\rho_2 = \rho_1/2$). The overflow experiment in the interferometer with the cells in series involves changing the density but not the amount of the gas in the measuring beam. Thus, the first-order effect of density is eliminated and one measures differentially the effect of molecular interactions on the refractivity of gases, indicated as the fringe count ΔK. In the second interferometer with the cells in parallel, the changes of density take place in different beams, thereby avoiding the elimination of the first-order effect of density during the overflow experiment. Thus, it measures the total fringe count K_1, which corresponds to a change of density between zero (initially evacuated cell) and ρ_1 of the initially filled cell. The coupled interferometers make it possible to obtain the dependent variable ΔK and the independent variable K simultaneously during the overflow experiment (*3*). It is self-evident that the contribution of the second, third, ... terms of the LL expansion depends on the range of density. One should therefore carry out the overflow experiments at least up to the same density as was used for the absolute measurements of $n(P,T)$.

Materials. The methane used for the measurements was supplied by Messer Griesheim, Germany (purity, $x(CH_4) >$ 0.999 995 where x denotes mole fraction; impurities, $x(O_2) \leq 0.5 \times 10^{-6}$, $x(N_2) \leq 2 \times 10^{-6}$, $x(H_2O) \leq 2 \times 10^{-6}$, $x(CO_2) \leq 0.1 \times 10^{-6}$, x(hydrocarbons) $\leq 0.1 \times 10^{-6}$).

Results and Discussion

Refractive Index. Measurements of $n(P,T)$ were carried out on the six isotherms at 273.15, 283.15, 293.15, 323.15, 348.15, and 373.15 K and pressures up to 34 MPa. Refractive indices $n(P,T)$ were calculated from the total interference fringe count $K_n(P,T)$ of the interferometer filled with methane by means of the formula

$$n(P,T) = K_n(P,T)\lambda_0/l + 1 \tag{2}$$

where λ_0 is the vacuum wavelength of the laser light and l is the spacer length at the actual temperature T of the sample. The pressure P was calculated from the interference fringe count K_P of the second interferometer filled with nitrogen using the previously established relation (*6*)

$$P = P(K_P, T_0) \tag{3}$$

The interferometric pressure determination enabled us to measure the refractive index $n(P,T)$ at predetermined even values of pressure (*2*). This had the advantage that all the measurements of methane on the different isotherms could be carried out within the experimental error on the same

Table II. Experimental Values of the Refractivity Virial Coefficients A_R, B_R, and C_R for Methane at the Vacuum Wavelength of λ_0 = 632.99 nm, Except for the Values from Olson (7) (λ = 546.2 nm)

T/K	A_R/(cm^3 mol^{-1})	B_R/(cm^6 mol^{-2})	C_R/(cm^9 mol^{-3})	ref
220	6.613 ± 0.002	6.1 ± 1.0	−320	7
298	6.578 ± 0.002	6.14 ± 0.20	−345 ± 15	8
323	6.576 ± 0.002	6.08 ± 0.10	−324 ± 5	3
373	6.576 ± 0.002	6.13 ± 0.15	−317 ± 10	3
273	6.5724 ± 0.0015	6.0[a]	−324[a]	this work
283	6.5741 ± 0.0015	6.0[a]	−324[a]	this work
293	6.5750 ± 0.0015	6.0[a]	−324[a]	this work
323	6.5762 ± 0.0015	6.0 ± 0.1	−324 ± 5	this work
348	6.5780 ± 0.0015	6.0[a]	−324[a]	this work
373	6.5770 ± 0.0015	6.0[a]	−324[a]	this work

[a] Estimated on the basis of the temperature independence of the B_R and C_R values within the range of temperatures from 220 to 373 K.

pressure series. The measured $n(P,T)$ values for pure methane are listed in Table I. The experimental uncertainties of the single values of n, P, and T were estimated in detail in a previous paper (1). The uncertainty of the refractive index measurement was estimated to be less than $\pm 5 \times 10^{-7}$ at 1 MPa and $\pm 5 \times 10^{-6}$ at 34 MPa. The uncertainty in pressure was less than $\pm 1.5 \times 10^{-4}$ for pressures from 0.6 MPa up to 35 MPa. The temperature was measured and controlled using platinum resistance thermometers and mercury thermometers. The uncertainty of the temperature measurements is ±0.01 K. The temperatures are reported on IPTS-68 for all experiments.

First Refractivity Virial Coefficient. The first refractivity virial coefficient A_R can be determined directly from isothermal n, P, and T measurements. The density ρ in eq 1 is replaced by the use of the compression factor Z

$$Z = P/\rho RT \tag{4}$$

where R is the molar gas constant, with the latest value given by R = 8.314 471 ± 0.000 014 J K^{-1} mol^{-1}. This leads to the relation

$$\frac{RT}{P}\frac{n^2-1}{n^2+2} = \frac{A_R}{Z} + \frac{B_R}{Z^2}\left(\frac{P}{RT}\right) + \frac{C_R}{Z^3}\left(\frac{P}{RT}\right)^2 + \ldots \tag{5}$$

The left side of eq 5 is plotted against P, and A_R is finally determined from the intercept.

The experimental values of $RT(n^2 - 1)/[(n^2 + 2)P]$ were plotted against P for each measurement run, and the coefficient A_R was determined from the intercept by using a least-squares fit. Table II includes the present experimental values of A_R with its uncertainty for the six investigated isotherms; A_R is weakly temperature dependent, and it increases slightly (0.1%) with increasing temperature between 273.15 and 373.15 K.

Higher-Order Refractivity Virial Coefficients. Overflow experiments for the measurement of the higher-order refractivity virial coefficients B_R, C_R, ... were carried out on pure methane on the 323.15 K isotherm at pressures up to 35 MPa. Procedures of the data treatment of $\Delta K(K,T)$ for the determination of B_R, C_R, ... have been discussed elsewhere (3). B_R and C_R are the only significant coefficients in the investigated range of pressures. The results of B_R and C_R and the standard deviation are given in Table II. For comparison, experimental values from the literature are also given in Table II. The values do not show any significant temperature dependence in the wide range of temperatures from 220 to 373.15 K.

Density. Molar densities were determined from the Lorentz–Lorenz expansion by solving eq 1 directly. Each isothermal expansion run yields an A_R value which was used

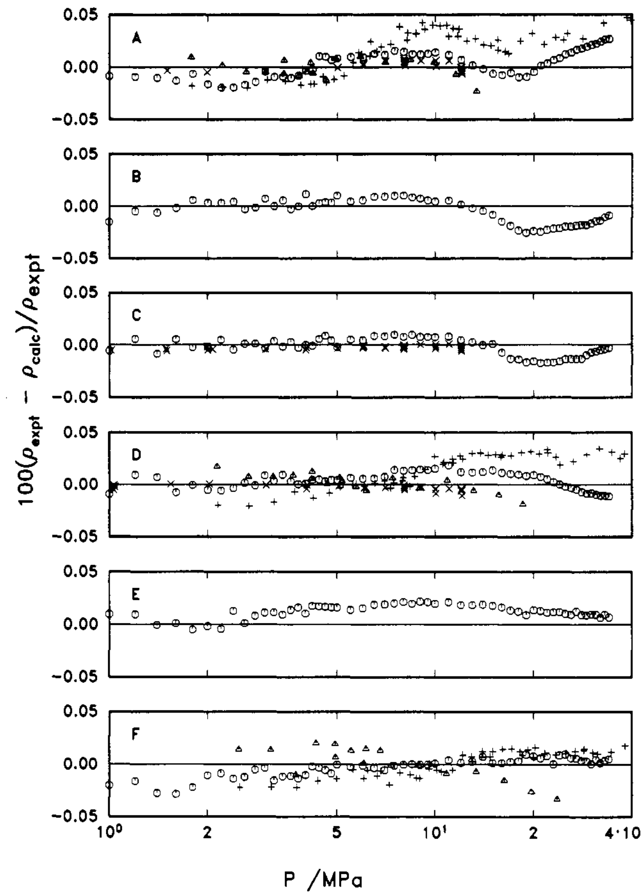

Figure 1. Relative deviation of calculated densities ρ_{calc} using the Setzmann and Wagner (5) equation of state from experimental values ρ_{expt}: O, this work; $\triangle$, Schamp et al. (9); $\times$, Pieperbeck et al. (10); +, Trappeniers et al. (11); A, 273.15 K; B, 283.15 K; C, 293.15 K; D, 323.15 K; E, 348.15 K; F, 373.15 K.

for the calculation of the density isotherm together with the B_R and C_R values at 323.15 K given in Table II. The corresponding $\rho(P,T)$ values calculated from the $n(P,T)$ measurements are listed in Table I. Figure 1 shows a comparison of the experimental results of this work with the selected measurements of three other researchers: Schamp et al. (9), Pieperbeck et al. (10), and Trappeniers et al. (11). The calculated relative deviations $100(\rho_{expt} - \rho_{calc})/\rho_{expt}$ do not exceed ±0.05%, and the deviations among the experimental values are mostly within ±0.03%. To avoid too much overlapping of our experimental points, only each second one is plotted. The deviations in Figure 1 are slightly different from the corresponding deviation plots given by Setzmann and Wagner (5) because improved values for B_R and C_R were available in our work. The uncertainty in density for the pressure of 1 MPa was estimated to be approximately ±0.02%, which is mainly established by the uncertainty of A_R, whereas at 34 MPa the estimated uncertainty of ±0.05% is established by the uncertainties of A_R, B_R, and C_R, but the uncertainties of B_R and C_R are predominant.

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