

Dielectric Constant of Compressed Gaseous and Liquid Oxygen*

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The dielectric constants of compressed gaseous and liquid oxygen were measured on ten isotherms at temperatures between 100 and 300 K and on the saturated liquid boundary at temperatures between 55 and 154 K. Densities ranged from 0.06 to 1.30 g/cm³ at pressures up to 33 MN/m². The dielectric constant measurements were combined with accurate density data to compute the Clausius-Mossotti (CM) function, $\left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{1}{\rho}$. The CM function for oxygen decreases with density from a value of 0.1236 cm³/g at the low density limit to 0.1219 cm³/g near the triple point.

Key words: Clausius-Mossotti function; dielectric constant; oxygen.

1. Introduction

Very precise measurements of the dielectric constants of compressed gases and liquids, in principle, can give important information about the nature of molecular interactions. Also, density metering of fluids can be performed accurately and quickly by capacitance measurements when the dielectric constant as a function of density is known. Although such measurements have been reported for a number of simple fluids [1–6],¹ no accurate wide-range measurements of compressed oxygen have yet been reported. This paper presents accurate dielectric constant measurements and derived values of the Clausius-Mossotti function $\left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{1}{\rho}$ for oxygen at pressures from the dilute gas to nearly three times the critical density and at temperatures between the triple point of the fluid (54.35 K) and 300 K.

2. Experimental Method

The dielectric constant was determined from the ratio of the capacitance when the cell was filled with fluid to the capacitance of the evacuated cell. The capacitor is essentially two coaxial cylinders of copper with the ends bearing on a common surface with three point contact in order to obtain high stability. Once assembled, the capacitor reproduced its vacuum capacitance versus temperature curve to within 1

part in 10⁵ after temperature cycling to 55 K and pressure cycling to 34 MN/m² (~5000 psi). A detailed description of the capacitor, as used here, is given in reference [7].

The capacitance was measured with a commercial three-terminal a-c bridge, using tapped transformer windings in the ratio arms. The outer cylinder was operated at 10 V and 5 kHz, and the inner cylinder was connected to the detector side of the bridge. The bearing surfaces, sample holder, and outer conductor of the coaxial leads, and the bridge shield were grounded to form the third lead in the usual three-terminal connection for capacitance measurements.

2.1. Cryostat

The cryostat was all-metal construction, using liquid nitrogen as the refrigerant. The design is essentially that of Goodwin [8].

2.2. Sample Holder and Sample

The sample holder was made of electrolytic tough pitch copper. The sample temperature was regulated by nulling the platinum resistance thermometer emf against a fixed setting on a six dial potentiometer. The guard ring temperature was regulated to the sample temperature using a copper versus gold-cobalt thermocouple in a power control loop.

The sample was laboratory grade oxygen whose impurities, according to the supplier's specifications, were 17 ppm argon, 12 ppm hydrocarbon, 11 ppm krypton, 10 ppm nitrogen, and 2 ppm water. This would contribute less than 0.01 percent to the polarizability. Even so, the sample was further purified by passing it through a silica gel trap at 77 K.

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

2.3. Temperature, Pressure, and Density Measurements

The temperature was measured with a 25 Ω platinum resistance thermometer calibrated on the NBS-1955 and IPTS 1948 by the NBS Temperature Section. Adjustment to the IPTS 1968 can be made via reference [9]. The difference in CM, which results from neglecting the difference in the 1968 and 1948 scale, is small, usually much less than 0.2 percent. The calibration of the thermometer was checked periodically by measuring the vapor pressures of oxygen. The temperatures calculated from the vapor pressure measurements, using the tables of Weber [10], were within 4 millidegrees of that indicated by the thermometer calibration. Pressure measurements were made with a deadweight gage which communicates with the sample holder through a 0.056 cm i.d. stainless-steel capillary. Sensitivity of the pressure measurements were of the order of 10^{-4} MN/m²; the accuracy uncertainty was about twice that of the sensitivity.

The fluid densities were determined from temperature and pressure measurements and the PVT surface of Weber [10]. Uncertainties in the densities were believed to be less than 1 part in 1000, except when within a few degrees of the critical temperature.

Near the critical point the densities may be in error by as much as 1 or 2 percent.

TABLE 1. *Coefficients of Eqs (1) and (2)*

Eq. (1)		Eq. (2)	
<i>A</i>	0.12361 (1) cm ³ /g	0.12378 (2) cm ³ /g	
<i>B</i>	.00032 (4) cm ⁶ /g ²	.00029 (3) cm ⁶ /g ²	
<i>C</i>	-.00121 (3) cm ⁹ /g ³	-.00126 (2) cm ⁹ /g ³	
<i>D</i>		-.00000067 (9) cm ³ /g K	
σ	.000038 cm ³ /g	.000032 cm ³ /g	

A, *B*, *C*, and *D*, are coefficients for eqs (1) and (2); numbers in parentheses are estimated imprecision in the last digit of the coefficients, σ is the rms deviation.

3. Results and Discussions

Measurements of dielectric constant, ϵ , in the compressed fluid as a function of pressure or density on isotherms, with the corresponding values of CM are listed in table 2.

Experimental values ϵ at saturation (previously reported [14]) are given in table 3.

Table 2. *Dielectric constant measurements and Clausius-Mossotti function of compressed fluid oxygen*

The densities were calculated from reference [10], using pressure and temperature as entries.

ρ g/cm ³	CM cm ³ /g	ϵ	<i>T</i> K	<i>P</i> MN/m ²	ρ g/cm ³	CM cm ³ /g	ϵ	<i>T</i> K	<i>P</i> MN/m ²
0.11189	0.12359	1.04207	300.0	8.357	.50289	.12343	1.19854	240.0	26.930
.09715	.12359	1.03646	300.0	7.285	.46111	.12346	1.18109	240.0	24.060
.08547	.12361	1.03203	300.0	6.432	.64417	.12333	1.25891	220.0	32.381
.07743	.12361	1.02899	300.0	5.842	.59875	.12334	1.23922	220.0	28.225
.06884	.12361	1.02575	300.0	5.210	.54679	.12343	1.21712	220.0	24.416
.05944	.12362	1.02221	300.0	4.514	.50155	.12347	1.19804	220.0	21.688
.05748	.12362	1.02147	300.0	4.368	.45605	.12350	1.17904	220.0	19.348
.05057	.12363	1.01887	300.0	3.853	.41352	.12353	1.16149	220.0	17.426
.42831	.12344	1.16747	280.0	29.929	.35296	.12359	1.13683	220.0	14.975
.32336	.12352	1.12481	280.0	21.660	.30203	.12360	1.11634	220.0	13.055
					.19101	.12359	1.07253	220.0	8.893
.25453	.12355	1.09740	280.0	16.934	.16248	.12361	1.06149	220.0	7.760
.19988	.12357	1.07598	280.0	13.367	.14137	.12363	1.05337	220.0	6.889
.47979	.12342	1.18883	260.0	30.045	.12719	.12364	1.04793	220.0	6.287
.44900	.12343	1.17602	260.0	27.557	.10949	.12365	1.04117	220.0	5.512
.39978	.12351	1.15583	260.0	23.972					
.35279	.12354	1.13672	260.0	20.885	.73510	.12309	1.29846	200.0	32.977
.31750	.12355	1.12249	260.0	18.720	.69060	.12325	1.27910	200.0	28.096
.25405	.12360	1.09725	260.0	15.041	.58556	.12342	1.23370	200.0	20.355
.20062	.12363	1.07630	260.0	12.042	.52454	.12348	1.20777	200.0	17.436
.13218	.12362	1.04984	260.0	8.173	.47881	.12351	1.18856	200.0	15.704
.12154	.12363	1.04577	260.0	7.558	.42090	.12356	1.16458	200.0	13.864
.10563	.12366	1.03970	260.0	6.628	.37127	.12359	1.14428	200.0	12.473
.07741	.12364	1.02899	260.0	4.943	.31196	.12360	1.12031	200.0	10.906
.05646	.12364	1.02109	260.0	3.656	.26489	.12363	1.10157	200.0	9.662
.54269	.12341	1.21535	240.0	30.066	.23176	.12355	1.08843	200.0	8.753

TABLE 2. Dielectric constant measurements and Clausius-Mossotti function of compressed fluid oxygen—Continued

ρ g/cm ³	CM cm ³ /g	ϵ	T k	P MN/m ²	ρ g/cm ³	CM cm ³ /g	ϵ	T K	P MN/m ²
0.21411	0.12362	1.08156	200.0	8.249	.09240	.12363	1.03467	160.0	3.030
.17476	.12365	1.06626	200.0	7.063	.05678	.12362	1.02121	160.0	2.044
.14312	.12363	1.05404	200.0	6.028	1.00036	.12260	1.41937	140.0	32.781
.15121	.12364	1.05715	200.0	6.301	0.96157	.12274	1.40146	140.0	22.396
.11825	.12366	1.04452	200.0	5.153	.95619	.12276	1.39899	140.0	21.171
.09658	.12369	1.03627	200.0	4.340	.94614	.12280	1.39438	140.0	19.011
.07901	.12370	1.02961	200.0	3.643	.93411	.12284	1.38887	140.0	16.638
.06087	.12371	1.02276	200.0	2.882	.92091	.12289	1.38282	140.0	14.281
.82534	.12298	1.33888	180.0	33.059	.90835	.12292	1.37707	140.0	12.264
.90737	.12281	1.37623	160.0	31.425	.89131	.12297	1.36928	140.0	9.852
.85543	.12300	1.35278	160.0	22.265	.87299	.12302	1.36094	140.0	7.643
.83368	.12306	1.34296	160.0	19.323	.83125	.12307	1.34187	140.0	3.910
.80273	.12313	1.32903	160.0	15.907	1.06595	.12249	1.45052	120.0	26.000
.75569	.12321	1.30800	160.0	12.142	1.03038	.12265	1.43397	120.0	14.194
.70663	.12328	1.28629	160.0	9.608	1.02298	.12267	1.43050	120.0	12.099
.65984	.12336	1.26584	160.0	8.119	1.01174	.12271	1.42523	120.0	9.136
.61350	.12344	1.24582	160.0	7.237	1.00032	.12274	1.41989	120.0	6.393
.55699	.12350	1.22162	160.0	6.644	0.98732	.12277	1.41380	120.0	3.579
.51907	.12351	1.20551	160.0	6.418	1.11997	.12242	1.47670	100.0	11.648
.40624	.12358	1.15857	160.0	6.048	1.10948	.12246	1.47171	100.0	7.287
.33530	.12357	1.12968	160.0	5.835	1.10182	.12249	1.46807	100.0	4.302
.29645	.12364	1.11415	160.0	5.670	1.09418	.12252	1.46443	100.0	1.490
.25265	.12364	1.09673	160.0	5.405					
.19693	.12366	1.07488	160.0	4.884					
.15111	.12368	1.05714	160.0	4.239					

TABLE 3. Dielectric constant of saturated liquid oxygen

The densities were calculated from reference [10] using temperature as an entry.

T K	ρ g/cm ³	ϵ	CM cm ³ /g	T K	ρ g/cm ³	ϵ	CM cm ³ /g
54.478	1.3066	1.56848	0.12192	114.000	1.0117	1.42522	.12270
55.000	1.3038	1.56740	.12199	118.000	.9869	1.41356	.12276
56.000	1.2993	1.56510	.12199	120.000	.9740	1.40751	.12279
62.000	1.2728	1.55178	.12206	122.000	.9607	1.40132	.12282
64.000	1.2638	1.54731	.12209	124.000	.9469	1.39488	.12283
68.000	1.2458	1.53835	.12213	126.000	.9327	1.38828	.12286
72.000	1.2276	1.52935	.12218	128.000	.9180	1.38152	.12291
76.000	1.2091	1.52026	.12224	130.000	.9026	1.37440	.12293
80.000	1.1903	1.51108	.12229	134.000	.8698	1.35939	.12300
84.000	1.1712	1.50179	.12235	138.000	.8333	1.34282	.12306
88.000	1.1518	1.49242	.12242	142.000	.7916	1.32400	.12313
92.000	1.1319	1.48272	.12245	146.000	.7416	1.30164	.12320
96.000	1.1116	1.47285	.12249	148.000	.7114	1.28828	.12323
100.000	1.0907	1.46280	.12254	150.000	.6755	1.27244	.12325
102.000	1.0800	1.45769	.12256	152.000	.6291	1.25206	.12320
104.000	1.0691	1.45250	.12259	153.000	.5980	1.23804	.12294
106.000	1.0581	1.44723	.12261	153.500	.5783	1.22904	.12265
108.000	1.0469	1.44188	.12263	154.000	.5533	1.21646	.12163
110.000	1.0354	1.43637	.12264				
112.000	1.0237	1.43089	.12268				

The Clausius-Mossotti function can be empirically represented by a polynomial in density,

$$CM \equiv \left(\frac{\epsilon - 1}{\epsilon + 2} \right) \frac{1}{\rho} = A + B\rho + C\rho^2. \quad (1)$$

The rms deviation of our measurements from eq (1) is 3.8×10^{-5} cm³/g, or about 0.028 percent in CM.

The departures of the compressed liquid isotherms from the saturated liquid curve, although not large, are believed to be a real effect. An addition of a linear term in temperature accounts for them quite well, i.e.,

$$CM = A + B\rho + C\rho^2 + DT. \quad (2)$$

The rms deviation of our measurements from eq (2)² is then 3.2×10^{-5} cm³/g in CM (0.03 percent).

Equation (1) may be inverted mathematically to give density as a function of the dielectric constant, providing a practical way to determine accurate fluid densities from capacitance measurements.

The low density limit of CM, i.e., the constant *A* of eq (1), is the polarizability of the isolated oxygen molecule. As yet this quantity has not been calculated theoretically. However, accurate dielectric constant measurements of Dunn [11] at standard temperature and pressure of O₂ (at $\rho = 0.0013$ g/cm³) allows a check. His data when converted to CM differ from our measurements by 0.14 percent. This should be the upper limit of the uncertainty in CM, since it occurs at low density where the uncertainty is largest.

The appearance of figure 1 suggests that the second dielectric virial coefficient *B* might be negative. However, the overall fit of the data to eq (2) indicated that *B* is positive though small. Negative values for *B* have been found for He [4] and Ne [5], which have caused difficulties for the theorists. Levine and McQuarrie [12] point out that although the form of the correct theory for *B* is known, due to lack of knowledge of how the polarizability of a pair of molecules vary as a function of their separation, the usual simplification was to assume a constant polarization which is asymptotically valid in the limit of large separation. The result is that the predicted values of *B* are always positive. Other words of discouragement have been expressed by Jansen [13]. He attempted to account for the density variations of the dielectric constant from a quantum mechanical basis, starting from the Lorenz microscopic field equations with the concept of a local field. He concludes that such a theory is fundamentally ineffective in accounting for the experimental results within their accuracy, even at low densities.

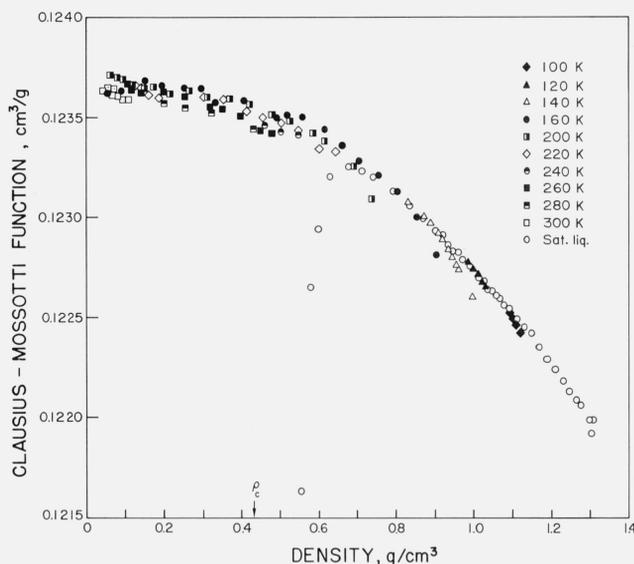


FIGURE 1. *CM* function versus density for oxygen.

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²The coefficients are given in table 1.