

FIG. 1. Clausius-Mosotti function for ethylene at 25°C.

series of observations the gas condenser was evacuated and its capacity in this state checked. Throughout the measurements this value did not vary by more than $\pm 0.03 \mu\text{mf}$.

The change in the condenser dimensions with pressure was shown by calculation to cause negligible error in the capacity measurements even at the highest pressures.

RESULTS

In order to determine densities from measured pressures the $P-V-T$ data of Michels and Geldermans²⁰ for ethylene were used. To convert the values of Amagat density so obtained to densities in moles/liter the normal volume is required. This was calculated from the relationship,

$$V_n = 22.414/(1+\lambda) \text{ liters,} \quad (1)$$

using the value of λ found by Cawood and Patterson.²¹ The figure obtained was 22.251 liters.

The values of the Clausius-Mosotti function are shown in Tables I and II and in Figs. 1 and 2 for the temperatures 25°C and 50°C. For convenience in extrapolation an attempt was made to fit the low density values by a least squares analysis to an expression of the form,

$$(\epsilon-1)/(\epsilon+2)d = A + Bd + Cd^2, \quad (2)$$

d being the density and A , B , and C constants for a given temperature. A reasonable fit was impossible for the 25°C values but was achieved at 50°C with the constants:

$$A = 10.69 \pm 0.01 \text{ cm}^3 \text{ mole}^{-1}$$

$$B = 25 \pm 7 \text{ cm}^6 \text{ mole}^{-2}$$

$$C = 540 \pm 820 \text{ cm}^9 \text{ mole}^{-3}.$$

The curve corresponding to these values is shown in Fig. 2.

²⁰ A. Michels and M. Geldermans, *Physica* 9, 967 (1942).

²¹ W. Cawood and H. S. Patterson, *J. Chem. Soc.* 619 (1933).

It will be noticed that the experimental points do not strictly lie on a smooth curve, but rather on a periodic curve superimposed on a smooth curve. For example, in our results there is a positive "peak" at density 0.002 mole/cc and a negative "peak" at density 0.004 moles/cc on each curve. This phenomenon is noticeable in the results of other workers, e.g., Michels and Kleerekoper³ for CO_2 and Keyes *et al*² for CH_4 , N_2 , CO_2 , and NH_3 .

The evident agreement between the zero-density values of the Clausius-Mosotti function at the two temperatures (see Figs. 1 and 2) is in accord with the known absence of dipole moment in ethylene. The value (10.69) deduced from these measurements agrees well

TABLE I. Clausius-Mosotti function for ethylene at 25.00°C.

Pressure (int. atmos)	Density (moles/liter)	Dielectric constant	Clausius-Mosotti function (cc/mole)
21.696	1.0262	1.0332	10.680
28.221	1.4121	1.0461	10.708
35.593	1.9187	1.0631	10.737
45.530	2.7894	1.0926	10.733
46.209	2.8621	1.0951	10.740
54.615	3.9657	1.1337	10.760
55.083	4.0438	1.1366	10.772
59.263	4.8685	1.1666	10.804
60.606	5.1959	1.1790	10.836
62.426	5.7033	1.1985	10.881
64.491	6.3823	1.2251	10.937
64.924	6.5386	1.2311	10.938
66.888	7.2822	1.2602	10.960
66.908	7.2899	1.2603	10.954
67.930	7.6769	1.2748	10.930
72.839	9.146	1.3316	10.881
80.368	10.359	1.3809	10.876
94.287	11.524	1.4297	10.872
94.564	11.541	1.4303	10.868
125.62	12.851	1.4859	10.846
125.89	12.860	1.4862	10.845
181.59	14.092	1.5402	10.829
272.12	15.247	1.5925	10.816
385.54	16.193	1.6364	10.807
534.27	17.082	1.6778	10.789

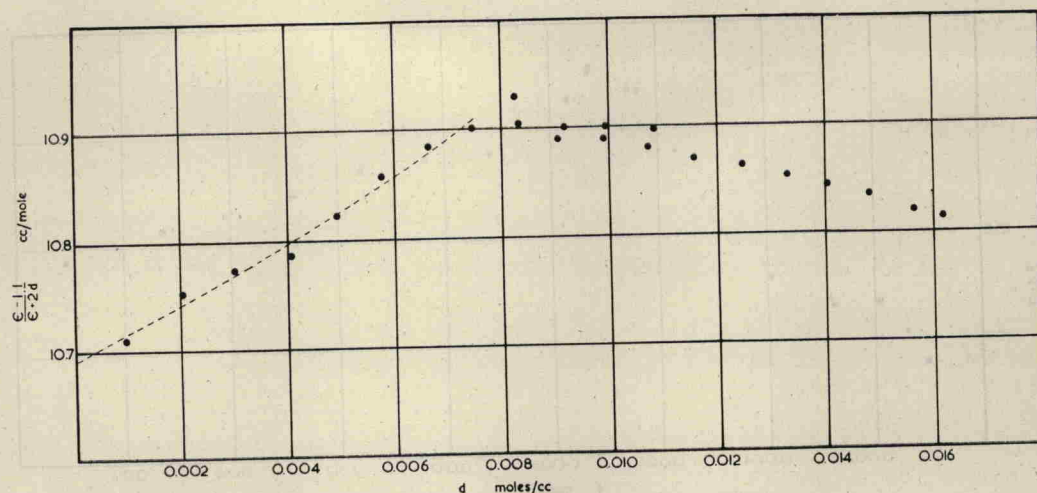


FIG. 2. Clausius-Mosotti function for ethylene at 50°C.

with the existing data²² for 25°C, *viz.*:

Boltzmann	(1874)	9.74 cc/mole
Klemencic	(1885)	10.81 cc/mole
Smyth and Zahn	(1925)	10.72 cc/mole
Watson, Rao, and Ramaswamy	(1934)	10.74 cc/mole

DISCUSSION

The C-M relationship may be written in the form,

$$(\epsilon-1)/(\epsilon+2)d = 4\pi\alpha N/3, \quad (3)$$

where ϵ is the dielectric constant of a substance, d is its density in molar units, α is its molecular polarizability and N is Avogadro's number. If α is assumed to be constant the C-M function, $(\epsilon-1)/(\epsilon+2)d$, should also

TABLE II. Clausius-Mosotti function for ethylene at 50.00°C.

Pressure (int. atmos)	Density (moles/liter)	Dielectric constant	Clausius-Mosotti function (cc/mole)
23.527	0.9980	1.0324	10.711
42.234	2.0181	1.0665	10.753
56.186	3.0007	1.1002	10.774
67.851	4.0529	1.1372	10.787
75.783	4.9229	1.1688	10.823
82.733	5.7899	1.2013	10.859
89.241	6.6510	1.2342	10.886
95.683	7.4839	1.2665	10.902
102.42	8.2699	1.2981	10.931
102.87	8.3177	1.2993	10.906
110.32	9.045	1.3278	10.891
112.05	9.194	1.3342	10.902
121.50	9.900	1.3626	10.891
121.97	9.931	1.3643	10.902
135.96	10.721	1.3962	10.882
138.62	10.846	1.4021	10.899
157.39	11.593	1.4327	10.872
188.48	12.480	1.4706	10.865
229.19	13.304	1.5064	10.855
277.71	14.029	1.5384	10.846
347.23	14.808	1.5735	10.837
448.26	15.653	1.6118	10.821
529.43	16.186	1.6366	10.815

²² Summarized by Watson, Rao, and Ramaswamy, Proc. Roy. Soc. (London) A143, 558 (1934).

be constant. It has been found experimentally, however, that the function is to some extent dependent on density. Explanations of this effect have been based upon two considerations: (a) that α may vary with density,⁶ (b) that the Lorentz molecular model is not applicable at high densities and the equality (3) does not necessarily hold.^{4,5,7,8} No quantitative information has yet been provided by the first approach and we shall consider our results in the light of the theory which Kirkwood developed to replace the Lorentz derivation of Eq. 3.

Kirkwood⁴ determined statistically the effect of translational fluctuations on the average local electric field in a molecule and obtained an expression of the form:

$$(\epsilon-1)/(\epsilon+2)d = P_0(1 + \gamma P_0 d + \delta P_0^2 d^2 + \dots) \quad (4)$$

where d is the density of the gas and P_0 is its molar polarization at zero density. He showed that the coefficient γ is given by

$$\gamma = (P_0/b)[1 + (A/3bRT)] \quad (5)$$

in the special case of a gas consisting of hard spherical molecules with mutual attractive potentials, $V(r)$, which vary inversely as the sixth power of the intermolecular distance, r . A and b are the constants of the van der Waals equation of state.

There is some uncertainty as to the values that should be used for A and b in Eq. (4) and the adequacy of the van der Waals type of intermolecular field is, in any case, rather doubtful.² For these reasons we have calculated γ from equations based upon the more accurate representation of intermolecular forces which is given by the Lennard-Jones²³ expression:

$$V(\rho) = 4E^*(\rho^{-12} - \rho^{-6}) \quad (6)$$

$$\rho = r/r_0.$$

²³ J. E. Lennard-Jones, Proc. Roy. Soc. (London) A106, 463 (1924).