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## The Dielectric Constant of Ethylene at High Pressures

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The dielectric constant of ethylene has been measured at pressures up to 500 atmospheres and at temperatures of 25°C and 50°C. At both temperatures the Clausius-Mosotti function has been found to pass through a maximum with increasing density. The results have been discussed with reference to Kirkwood's theory of dielectric polarization.

### INTRODUCTION

THE study of the dielectric constant of gases over a wide range of densities is of interest in the development of theories of dielectric behavior. A review of work done in this field has been recently given by Miller.<sup>1</sup>

The Clausius-Mosotti (C-M) treatment requires that  $(\epsilon - 1)/(\epsilon + 2)d$ , where  $\epsilon$  and  $d$  are the dielectric constant and density of the gas respectively, should be independent of density. Also for gases with non-polar molecules, the C-M ratio should be independent of temperature. However, variations in the value of the C-M ratio with density have been found for carbon dioxide,<sup>2,3</sup> ammonia,<sup>4</sup> and propane.<sup>2</sup> Several authors have advanced explanations for these variations,<sup>4-8</sup> but the agreement between theory and experiment leaves much to be desired.

It was decided in this work to extend the range of experimental data by measuring the dielectric constant of ethylene at various densities and at temperatures of 25°C and 50°C, and to consider the implications of the results.

### APPARATUS

The procedure adopted for this study was to confine ethylene at a known temperature and various pressures between the plates of a gas condenser contained in a pressure vessel and to measure the capacity of the condenser and the pressure of the gas. To achieve this, it was necessary to have a supply of pure ethylene, a means of compressing it in the gas condenser, and equipment for accurately measuring temperature, pressure, and capacity.

#### Gas Condenser

The condenser and containing vessel were similar to those used by Michels.<sup>9</sup> The former consisted of two

concentric brass cylinders with the outer supported from the inner cylinder by silica disks. The outer cylinder was in electrical contact with the pressure vessel and connection with the inner cylinder was made through a low capacity insulated plug of the type described by Michels.<sup>9</sup> The design of the condenser was such as to ensure minimum distortion of the cylinders at high gas pressures.

The containing pressure vessel was made of high tensile steel. It was rigidly and independently supported in an oil thermostat. The capacity measuring equipment was mounted on the same support and a rigid coaxial lead connected the gas condenser to this equipment.

The temperature of the oil thermostat was maintained constant to  $\pm 0.005^\circ\text{C}$  by an electronic temperature controller (see Wylie).<sup>10</sup> It was measured by a Leeds and Northrup Platinum Resistance Thermometer and G-2 Mueller Bridge. The thermometer and bridge were calibrated by the U. S. National Bureau of Standards and the Ice Point resistance of the thermometer was determined in this laboratory.

#### Pressure Balance

The pressures were measured by a modified Budenberg-type Pressure Balance which has been described by one of the authors.<sup>11</sup> The balance was used in conjunction with a U-tube containing mercury and an oil injector as described by Keyes.<sup>12</sup> The pressures were measured over the whole range (20-530 atmospheres) with a piston-cylinder unit of nominal piston area of 0.02 sq. in. It was calibrated against the vapor pressure of carbon dioxide at 0°C (see Bridgman).<sup>13</sup> In this calibration it was found that a change in the weight on the piston of one part in 95,000 was sufficient to make or break contacts in the U-tube and readings were reproducible to one part in 25,000. The calibrated value of the gauge constant was assumed to be correct up to 530 atmospheres. Keyes<sup>12</sup> has shown this assumption to be justifiable.

<sup>10</sup> R. G. Wylie, Natl. Standards Lab. C.S.I.R.O. Report No. PA-2 (1948).

<sup>11</sup> J. F. Pearse, submitted for publication in J. Sci. Instr.

<sup>12</sup> F. G. Keyes, Proc. Am. Acad. Arts Sci. 68, 505 (1933).

<sup>13</sup> O. C. Bridgman, J. Am. Chem. Soc. 49, 1174 (1927).

<sup>1</sup> J. G. Miller, Trans. Am. Soc. Mech. Engrs. 70, 621 (1948).  
<sup>2</sup> F. G. Keyes and J. L. Oncley, Chem. Revs. 19, 195 (1936).  
<sup>3</sup> A. Michels and L. Kleerekoper, Physica 6, 586 (1939).  
<sup>4</sup> F. G. Keyes and J. G. Kirkwood, Phys. Rev. 36, 1570 (1930); 37, 202 (1931); J. G. Kirkwood, J. Chem. Phys. 4, 592 (1936).  
<sup>5</sup> J. H. Van Vleck, J. Chem. Phys. 5, 556, 991 (1937).  
<sup>6</sup> Michels, de Boer, and Bijl, Physica 4, 981 (1937).  
<sup>7</sup> C. J. F. Böttcher, Physica 9, 937, 945 (1942).  
<sup>8</sup> W. F. Brown, J. Chem. Phys. 18, 1193, 1200 (1950).  
<sup>9</sup> A. Michels and Mrs. C. Michels, Trans. Roy. Soc. (London) (A) 231, 409 (1933).

### Mercury Gas-Compressor

This unit was based on a design developed by Michels and described by Tongue.<sup>14</sup> It was used in conjunction with a "Cook" 3000 atmospheres two-stage pump.<sup>15</sup>

### Ethylene Storage Cylinder and Transfer Vessel

The gas was stored in a high tensile steel pressure vessel of one liter capacity. The transfer vessel, the use of which will be described later, was made of stainless steel and had a capacity of 150 ml.

### Electrical Equipment

The method used for capacity measurements was that described by P. Cohen Henriquez.<sup>16</sup> The circuit consisted of a pentode valve, type 6F6G, with a 1000 Kc quartz crystal controlling the grid circuit. The anode circuit was tuned by means of an inductance in parallel with the gas condenser and a standard variable condenser. The anode voltage was supplied by a stabilized power pack and the heater current was taken from a 6-volt battery. Such a circuit exhibits the usual minimum of anode current at the capacity corresponding to the natural frequency of the crystal with the important feature that the slope of the curve on the high capacitance side is very steep. A suitable operating point is chosen on the steepest portion of the curve and capacitance adjusted until the anode current is at the chosen value. To obviate errors in the capacity measurements caused by drifts in the oscillator circuit, a reference condenser was included, as suggested by P. Cohen Henriquez.<sup>16</sup>

The standard condenser was constructed from a transmitting condenser. The spindle, supported in a lapped conical bearing, was rotated by a worm and wheel drive fitted with an anti-backlash device. The worm spindle carried a graduated drum on which one division was equivalent to  $1/100 \mu\text{F}$ . The instrument was calibrated by the Division of Electrotechnology of the C.S.I.R.O. and found to be consistent to  $\pm 0.02 \mu\text{F}$  over a long period. The whole of the capacity measuring equipment was screened.

## EXPERIMENTAL PROCEDURE

### Preparation of Ethylene

The gas was prepared by the dehydration of ethyl alcohol by Pyro-phosphoric acid at 220–240°C. An apparatus was set up in which to carry out this preparation in a continuous manner. The alcohol was led into a flask containing 100 cc of Pyro-phosphoric acid (prepared *in situ* by dehydration of ortho-phosphoric acid) at the required temperature. The ethylene was passed successively at atmospheric pressure through a dry ice

and alcohol trap, a wash bottle containing concentrated sulfuric acid, another containing 50 percent caustic soda, a further dry ice and alcohol trap, and a liquid air trap in which it was finally condensed.

When sufficient gas had been collected in the last trap, production was ceased and the permanent gases were pumped off. The ethylene was then fractionally distilled in batches in a low temperature fractionating column similar to that described by Lu, Newitt, and Ruhemann.<sup>17</sup> The middle fractions of ethylene were condensed in the gas transfer vessel immersed in liquid air. The vessel was then warmed and the ethylene passed into the mercury gas-compressor and pumped into the gas storage cylinder. One hundred liters of ethylene were prepared. Before preparation and storage of the gas, the glass apparatus was pumped out at a pressure of less than  $1/10$ th micron and flamed and the gas compressor and vessels were pumped out for several days. A sample of the ethylene was analyzed and 99.7 percent by volume was adsorbed by bromine water. The residual gas was shown to be non-condensable at liquid air temperature.

### Calibration of Gas Condenser

The vacuum capacity of the gas condenser was determined in the usual way by calibration with benzene.<sup>18</sup> Carefully fractionated benzene, dried for several weeks over sodium, was refluxed and stored over sodium in a glass vessel. It was degassed and distilled in vacuum into the previously evacuated gas condenser. Mercury U-tube valves were used in the system to prevent contamination of the benzene by tap-grease.

The vacuum capacity at 25°C was found to be  $148.96 \pm 0.05 \mu\text{f}$  (taking  $\epsilon_{25} = 2.2725$  for benzene),<sup>19</sup> compared with the value  $149.4 \mu\text{f}$  calculated from the condenser dimensions. The change in capacity of the evacuated condenser between 25°C and 50°C was found to be  $+0.04 \mu\text{f}$  (calculated value,  $+0.07 \mu\text{f}$ ). Since this variation is smaller than the probable error in the calibration, the same value of the vacuum capacity was used at both temperatures.

### Capacity Measurements

The condenser was filled from the storage vessel (via the gas compressor) with ethylene at the desired pressure and temperature (25°C or 50°C). Readings of the standard condenser and pressure balance were taken when the values appeared constant. These were checked after an interval of five minutes to confirm that the system was in equilibrium. Measurements were made over a range of pressures, the points being chosen so that the capacity of the gas condenser changed in approximately equal steps ( $\approx 5 \mu\text{f}$ ). Before and after a

<sup>14</sup> H. Tongue, *The Design and Construction of High Pressure Plant* (Chapman and Hall, Ltd., London, 1934).

<sup>15</sup> D. M. Newitt, *High Pressure Plant and Fluids at High Pressures* (Oxford University, New York, 1940).

<sup>16</sup> P. Cohen Henriquez, *Physica* 2, 429 (1935).

<sup>17</sup> Lu, Newitt, and Ruhemann, *Proc. Roy. Soc. (London)* A178, 506 (1941).

<sup>18</sup> R. J. W. Le Fèvre, *Dipole Moments* (Methuen and Company, Ltd., London, 1938).

<sup>19</sup> L. Hartshorn and D. A. Oliver, *Proc. Roy. Soc. (London)* A123, 664 (1929).