have the same quantitative effects upon viscosity.

3. Another function of viscosity exists, $\Pi(\eta)$, or the "Π scale," which is generally additive in terms of pressure.

If viscosities are plotted in these functional scales, all normal or "ideal" additivity is represented as a straight line. Deviations from this course are very accurately recognizable and significant.

Thus, the ϕ diagrams reveal "non-ideal" conditions, *i. e.*, associative or dissociative tendencies which could not be detected by other means. Extrapolation into the critical region suggests important conclusions regarding state discontinuity. The Π scale shows the correct magnitude of the internal pressures of liquids which, according to this evidence, are characteristic for whole series of related substances.

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RECEIVED DECEMBER 30, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. X. Equipment for Measuring Dielectric Constants of Gases. The Polarity of Gaseous Monoalkyl Acetylenes

BY F. J. KRIEGER AND H. H. WENZKE

In order to determine accurately the low moments of the monoalkyl acetylenes it is necessary to abandon the method of solutions used in the previous papers of this series and employ the temperature variation method on the vapors of the materials to be investigated. This paper describes an apparatus for measuring the dielectric constants of gases and a method for determining their polarizations and gives data obtained for five homologs.

Description of Apparatus

The present apparatus for measuring the dielectric constants of gases was designed with a view to ruggedness and stability in operation. It is essentially a beat-frequency oscillator designed for measuring extremely small capacities with great accuracy. It offers as points of superiority over those described by Groves and Sugden[1] and by Zahn,[2] first, alternating current operation for convenience and maintained foolproof operation; second, excellent stability, combined with the comparison capacity method of eliminating residual drift, as mentioned by Zahn, but not used by Groves and Sugden; and, third, a direct-meter reading of zero beat which, because of precautions taken to eliminate entirely any tendency of the two oscillators in the circuit to "lock in," gives a much higher precision of setting than does either the resonance method of Groves and Sugden or the audible-beat method of Zahn.

Inspection of the circuit diagram, Fig. 1, indicates that the disposition of the circuit capacities, together with the capacity to be measured is similar to that used by Groves and Sugden. However, where they use the amplitude of the voltage developed at a particular point on a steep resonance curve as an indication of resonance, we use the heterodyne note between two oscillators. Frequency drift is eliminated by stabilizing one oscillator with a quartz crystal and furnishing the other oscillator with a suitable reference standard for correcting against the effect of drift should any occur.

Vacuum tube V_1, together with the inductance L_1, the capacity C_1, and the crystal X, form an oscillating circuit at a frequency of 500 kc. per second. The crystal is of the low temperature coefficient type and the oscillator is such that constancy may be assured to a precision of six cycles per degree C.

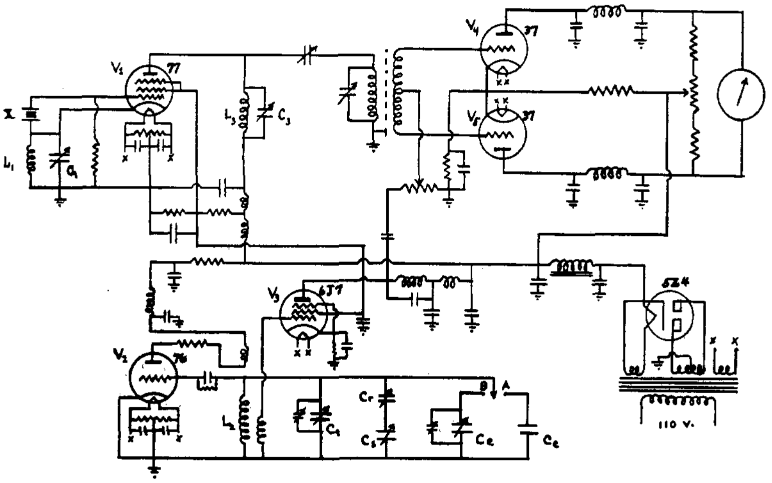

Fig. 1.—Circuit diagram of beat-frequency oscillator used in measuring dielectric constants of gases.

Vacuum tube V_2, the inductance L_2, and the capacities C_t, C_r, C_e and C_s, form the variable oscillator whose frequency is that of the second harmonic of the crystal oscil-

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(1) Groves and Sugden, *J. Chem. Soc.*, 1094 (1934).

(2) Zahn, *Phys. Rev.*, **24**, 400 (1924).

lator. This oscillator is isolated from the crystal-controlled oscillator and from the detector by radio frequency amplifier circuits associated with the buffer tube V_3.

Tubes V_4 and V_5 form a balanced detector system in which the second harmonic of the crystal-controlled oscillator beats with the output of the variable oscillator for the indication of circuit adjustment. This is always done at zero beat, indicated by the meter in the plate circuit of the detector tubes. By this means frequency differences as small as a fraction of a cycle per second may be detected easily.

The variable oscillator contains, as a part of its variable capacity, a General Radio standard condenser, C_s, in series with a small variable capacity, C_r. This arrangement makes possible a maximum sensitivity of 0.000267 mmf. (micromicrofarad) per division, over a total range of 0.56 mmf., while the lowest sensitivity is 0.00186 mmf. per division, over a total range of 3.92 mmf.

Thermal stability is achieved by two general methods. The first of these is the choice of component parts of very low temperature coefficients, and the second is a complete segregation of all tuning elements within a thermally-insulated chamber and thorough ventilation of all heat-producing units. These precautions result in a thermal stability such that the zero-beat adjustment drifted an average of 0.01 mmf. per hour. The effect of even this small drift is, in practice, eliminated by including in the circuit a capacity arrangement which can be set equal to the initial capacity of the circuit under test. By inserting this capacity, the oscillator may be returned to its original adjustment at any time.

The instrument is operated as follows:

(a) The switch is set at A and the gas cell is evacuated.

(b) The standard condenser, C_s, and the range condenser, C_r, are set at values which will accommodate the change in cell capacity that will occur upon the introduction of the gas under test. The dial readings of both condensers are recorded.

(c) The tank condenser, C_t, is tuned until the beat note as indicated in the meter is very low. The auxiliary condenser C_t vernier, is used to bring the beat note to a zero.

(d) The switch is thrown to B.

(e) The equivalent condenser, C_e, is tuned for zero beat. Any slight drift is eliminated by means of the auxiliary condenser C_e vernier.

(f) The switch is reset at A and the gas to be measured is introduced into the cell.

(g) The standard condenser, C_s, is readjusted accurately to zero beat. This value is recorded as C_s'.

(h) Should there be considerable delay between steps (e) and (g), the switch is thrown to B, and if the beat is no longer zero, condenser C_t vernier is readjusted to give exactly zero beat just before step (g) is carried out. Thus, the equivalent capacity, C_e, serves as a standard equal to the evacuated cell in capacity by means of which the oscillator may be readjusted at any time and its residual drift eliminated.

From the capacity values read in steps (b) and (g) the capacity change of the cell due to the introduction of the gas under test may be determined as follows. The total variable capacities must have been equal in the two cases to give the same frequency. Thus

$$C_c + C_t + \frac{C_rC_s}{C_r + C_s} = C_e + C_t + \frac{C_rC_s'}{C_r + C_s} + \Delta C_c$$

where ΔC_c is the change in cell capacity produced by the introduction of the gas. On simplifying the above equation and solving for ΔC_c we obtain

$$\Delta C_c = \frac{C_r^2(C_s - C_s')}{C_r^2 + C_c(C_s + C_s') + C_sC_s'} \qquad \text{(I)}$$

If we make use of the relation

$$\epsilon - 1 = \Delta C_c/C_c$$

where ϵ is the dielectric constant and C_c the replaceable cell capacity, we obtain the expression

$$\epsilon - 1 = \frac{C_r^2}{C_c}\,\frac{(C_s - C_s')}{C_c^2 + C_r(C_s + C_s') + C_sC_s'} \qquad \text{(II)}$$

This equation is identical in form with that of Groves and Sugden. It is to be noted that in their work these investigators neglect the term C_r^2 in the denominator, stating that C_r as it appears in the denominator need not be known very accurately. This statement is open to question as the capacity, C_r, has some effect on the third figure following the decimal point. It is also to be noted that neither end of the capacity, C_r, is at ground potential, and the determination of the capacity of any condenser when operated under such conditions is an indefinite matter when direct methods are used. The value of the capacity C_r may be obtained indirectly by the use of gases of known dielectric constant.

The dielectric constant gas cell consists of a Pyrex glass-enclosed condenser made of three concentric chromium-plated brass cylinders each 6″ (15.5 cm.) long and 3″ (7.6 cm.), 2³/₄″ (7.0 cm.) and 2¹/₂″ (6.35 cm.) in diameter, respectively, held rigidly in place by means of spring clips pressing against the outer glass wall. The outer and inner cylinders form one plate of the condenser which is maintained at ground potential. The condenser leads are of tungsten and are brought out at the top of the glass container. The top of the cell is furnished with a standard taper silver-clad joint to which is fitted a glass arm leading to a manometer, a vacuum pump and an inlet for the gases to be investigated. This arrangement is similar to that of Schwingel and Williams.[3]

The cell is mounted rigidly in a cottonseed oil-bath, the temperature of which is maintained

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[3] Schwingel and Williams, *Phys. Rev.*, **36**, 855 (1930).

within 0.02° of the desired temperature by means of a mercury thermoregulator and relay-controlled heater system. The cell is connected with the beat-frequency oscillator by means of a special rigid concentric cable whose outer sheath is grounded to prevent capacity losses. In order to prevent condensation of the higher-boiling materials in the glass arm and in the manometer, those parts were wrapped with Chromel-A resistance wire and brought to a suitable temperature by means of an electric current. This precaution permits the measurement of higher pressures of high-boiling materials than would be possible at room temperature.

Calibration of Apparatus

From equation (II) it is seen that, in order to determine the dielectric constant of the cell contents, it is necessary to know the apparatus constants C_r and C_r^2/C_c and the initial and final readings of the standard condenser C_s. The value of cell capacity, C_c, was determined in the following manner. After the gas cell was brought to constant temperature it was evacuated and the oscillator was brought to zero beat. This zero beat was maintained with the equivalent capacity, C_e, in the circuit. Meanwhile the external cell capacity was replaced by a General Radio standard condenser which was tuned to zero beat. The reading of this standard condenser gave the value of the external capacity from which the value of the cell capacity was deduced.

The value of the capacity C_r was determined indirectly by making observations with gases of known dielectric constant. For this purpose the measurements of Bryan and Sanders,[4] Stuart,[5] and Zahn[6] on air and carbon dioxide were employed. The mean polarization of air was taken as 4.368 cm.^{3} and that of carbon dioxide as 7.317 cm.^{3}. Assuming that the polarization of these gases does not change with temperature and that the gas laws hold, the dielectric constants of these gases at a known temperature and pressure may be calculated by means of the relation

$$\epsilon - 1 = 4.810 \times 10^{-5} P_M p/T \qquad \text{(III)}$$

where P_M is the molecular polarization, p the pressure in mm. of mercury, and T the absolute temperature.

The air used in the calibration was passed through a train consisting of bottles containing potassium hydroxide solution, concentrated sulfuric acid, calcium chloride and phosphorus pentoxide in that order. The carbon dioxide used was obtained from a cylinder of the liquefied gas. It was passed through concentrated sulfuric acid and dried over calcium chloride and phosphorus pentoxide.

The values of the dielectric constants of air and carbon dioxide at 25°, obtained by means of equation (III), were substituted into equation (II), which was then solved for the term C_r. The value of the capacity C_r, which was chosen small, was found to be 12.81 mmf. Since the capacity of the gas cell changed with the temperature, it was necessary to determine the apparatus constant, C_r^2/C_c, for each of the temperatures employed. As the value of C_r remained the same throughout, it was necessary only to find the values of C_c.

TABLE I

PRESSURES AND DIELECTRIC CONSTANTS OF CALIBRATING GASES AND CORRESPONDING VALUES OF APPARATUS CONSTANT AT 25°

p, mm.	$(\epsilon - 1) \times 10^4$	C_r, mmf.
	Air	
747.0	5.263	12.74
748.0	5.270	12.80
759.5	5.351	12.87
760.5	5.358	12.80
	Carbon Dioxide	
757.0	8.935	12.83
758.5	8.952	12.82
	Average	12.81

TABLE II

VALUES OF THE CELL CAPACITY AND OF THE APPARATUS CONSTANT AT TEMPERATURES INDICATED

	25°	75°	125°
C_c, mmf.	401.1	405.7	407.3
C_r^2/C_c	0.4089	0.4042	0.4027

Preparation of Materials.—The methyl- and ethylacetylenes were prepared by dropping the corresponding sulfates on sodium acetylide in liquid ammonia. The gas evolved was freed from ammonia by passing it through successive bottles of water and dilute sulfuric acid. The gaseous acetylenes were dried over calcium chloride and condensed by means of a dry ice–acetone bath. The liquid acetylenes were distilled through a Davis column,[7] recondensed, and

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[4] Bryan and Sanders. *Phys. Rev.*, **32**, 202 (1928).

[5] Stuart. *Z. Physik*, **47**, 457 (1928).

[6] Zahn, *Phys. Rev.*, **27**, 455 (1926).

[7] Davis and Daugherty. *Ind. Eng. Chem., Anal. Ed.*, **4**, 193 (1932).

stored in steel cylinders. The propyl-, butyl- and amylacetylenes were prepared by dropping the corresponding bromides on sodium acetylide in liquid ammonia. The acetylenes were distilled through a modified Widmer column.

TABLE III

PHYSICAL CONSTANTS OF ACETYLENES

Acetylene	B. p., °C.	d^{25}	$n^{25}\text{D}$	MR_{D}
Methyl	−23			14.04
Ethyl	7.9			18.66
Propyl	39.3	0.6909	1.38270	22.97
Butyl	71.0	.7146	1.39621	27.61
Amyl	98.0	.7297	1.40553	32.31

Technique and Results

The dielectric constants of the gases under consideration were determined by means of equation (II) at pressures, for the most part, above 100 mm. of mercury and at the three temperatures 25, 75, and 125°. In order to avoid the use of an equation of state for each of the gases in measuring its polarization, it was found expedient to plot $(\epsilon - 1)/p$ against p and extrapolate to zero pressure. The values of the dielectric constants and of the factors $(\epsilon - 1)/p$ are given in Tables IV, V and VI.

TABLE IV

PRESSURES, DIELECTRIC CONSTANTS AND POLARIZATION FACTORS OF MATERIALS AT 25°

p, mm.	$(\epsilon - 1) \times 10^4$	$((\epsilon - 1)/p) \times 10^6$
	Methylacetylene	
435.5	18.31	4.205
350.5	14.81	4.226
291.5	12.26	4.207
245.5	10.36	4.219
222.5	9.401	4.225
0		4.235
	Ethylacetylene	
480.0	24.70	5.145
391.0	20.10	5.140
287.0	14.77	5.146
269.5	13.93	5.169
180.5	9.339	5.174
0		5.205
	Propylacetylene	
320.0	19.88	6.214
273.5	17.02	6.223
230.5	14.35	6.227
178.0	11.08	6.225
130.5	8.152	6.246
0		6.260
	Butylacetylene	
86.0	6.173	7.178
74.5	5.337	7.164
70.0	4.976	7.110
48.5	3.485	7.185
0		7.153

TABLE V

PRESSURES, DIELECTRIC CONSTANTS AND POLARIZATION FACTORS OF MATERIALS AT 75°

p, mm.	$(\epsilon - 1) \times 10^4$	$((\epsilon - 1)/p) \times 10^6$
	Methylacetylene	
320.0	10.80	3.375
261.0	8.861	3.395
219.5	7.446	3.393
170.0	5.778	3.400
0		3.420
	Ethylacetylene	
486.5	19.47	4.002
411.5	16.51	4.014
327.0	13.23	4.051
227.5	9.229	4.056
144.0	5.865	4.073
0		4.100
	Propylacetylene	
314.0	15.07	4.798
306.5	14.73	4.807
235.0	11.38	4.841
188.0	9.118	4.850
136.5	6.662	4.880
0		4.930
	Butylacetylene	
237.5	13.37	5.632
151.0	8.551	5.663
109.5	6.225	5.685
97.5	5.537	5.679
0		5.725
	Amylacetylene	
209.5	13.15	6.275
152.5	9.60	6.295
104.0	6.578	6.325
0		6.350

The polarization at zero pressure and temperature T was obtained by multiplying the zero intercept, *i. e.*, $(\epsilon - 1)/p$ at $p = 0$, by $RT/3$ in accordance with the relation

$$P = \frac{\epsilon - 1}{\epsilon + 2} V = \frac{\epsilon - 1}{\epsilon + 2} \frac{RT}{p} = \frac{\epsilon - 1}{p} \frac{RT}{3} \qquad \text{(IV)}$$

where P is the polarization at temperature T, V the molar volume, p the pressure, R the gas constant and T the absolute temperature. The use of this perfect gas equation evidently is justified at zero pressure.

The electronic polarizations were obtained by determining experimentally the molar refraction for the sodium D line of propyl-, butyl- and amylacetylenes, and calculating the values for methyl- and ethylacetylenes on the basis of the refractions of their respective electron groups. As the

TABLE VI

PRESSURES, DIELECTRIC CONSTANTS AND POLARIZATION FACTORS OF MATERIALS AT 125°

p, mm.	$(\epsilon - 1) \times 10^4$	$((\epsilon - 1)/p) \times 10^6$
	Ethylacetylene	
351.0	11.55	3.290
263.0	8.918	3.391
201.0	6.982	3.474
195.5	6.501	3.325
164.0	5.736	3.497
0		3.440
	Propylacetylene	
345.5	14.09	4.079
295.0	12.15	4.120
215.5	8.837	4.101
174.0	7.168	4.119
0		4.115
	Butylacetylene	
258.5	12.09	4.677
210.0	9.832	4.682
141.0	6.616	4.692
114.0	5.353	4.696
0		4.712
	Amylacetylene	
173.5	8.955	5.161
149.0	7.710	5.174
120.0	6.219	5.183
0		5.245

TABLE VII

POLARIZATIONS OF MATERIALS AT INDICATED TEMPERATURES

Acetylene	25°	75°	125°
Methyl	26.26	24.76	...
Ethyl	32.27	29.68	28.48
Propyl	38.81	35.69	34.06
Butyl	44.35	41.41	39.01
Amyl	...	45.97	43.42

atomic polarizations could not be accurately determined, they were neglected in the calculations of the electric moments, which were obtained from the relation

$$\mu = 0.01273 \times 10^{-18}\sqrt{(P_T - P_E)T} \qquad \text{(V)}$$

where P_T is the total polarization, P_E is the electronic polarization and T the absolute temperature. The moments at the various temperatures and their mean values are given in Table VIII.

TABLE VIII

ELECTRIC MOMENTS OF ACETYLENES ($\mu \times 10^{18}$)

Acetylene	25°	75°	125°	Mean
Methyl	0.768	0.778	...	0.77
Ethyl	.811	.789	0.799	.80
Propyl	.875	.847	.846	.85
Butyl	.899	.882	.858	.87
Amyl	...	.878	.847	.86

Watson and Ramaswamy,[8] using the temperature variation method, obtained for the moment of methylacetylene the value 0.72, which agrees well with the value obtained by the authors, 0.77, considering that the small atomic polarization was neglected in the calculation of the latter value. The data of Table VIII indicate that the moment induced in the alkyl chain is negligible beyond the third carbon atom from the triple bond.

Summary

1. An apparatus has been constructed for measuring accurately the dielectric constants of gases and vapors at various pressures and temperatures.
2. A method which obviates the necessity of equations of state is used in determining the polarizations of gases and vapors from their dielectric constants.
3. The dielectric constants, polarizations and electric moments have been determined for gaseous methyl-, ethyl-, propyl-, butyl- and amylacetylenes.

NOTRE DAME, INDIANA RECEIVED APRIL 4, 1938

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[8] Watson and Ramaswamy, *Proc. Roy. Soc.*, **A156**, 130 (1936).