

Summary

The dielectric constants and densities of dilute solutions of the phenyl substituted ethylenes and acetylenes have been measured between 10 and 70°, the molar refractions of the substances have been determined and the data used to calculate the electric moments of the molecules.

The phenyl substituted ethylenes have small or zero moments according to the symmetry of their arrangement about the double bond, showing that there is no measurable polarity inherent in the bond itself. The replacement of a hydrogen on a doubly-bonded carbon by a hydrocarbon group gives rise to a moment of the same magnitude as that which results from a similar replacement in benzene.

The considerable moment found for phenylacetylene and the still larger value for diphenylacetylene, acetylene itself having no moment, give evidence of unsymmetrical molecules and may be explained in terms of a tautomeric equilibrium between a symmetrical form and an unsymmetrical containing bivalent carbon as proposed by Nef, the shift of equilibrium with temperature perhaps causing the temperature variation of the moment observed.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE EFFECT OF AN ELECTRIC FIELD ON FLAMES AND THEIR PROPAGATION¹

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RECEIVED JANUARY 27, 1931

PUBLISHED APRIL 6, 1931

The knowledge that flames conduct electricity goes back many years. As early as 1801, Volta showed that the leaves of a gold-leaf electroscope diverge when burning charcoal is brought in contact with the knob. Many researches followed for the purpose of measuring the electrical conductivity of flames. It was found that the gases which emerge from the flame are conductive for some time afterward and furthermore, that this property of conduction can be lessened or removed by passing the gases through an electric field of appropriate strength. Complete accounts of these early researches are to be found in Wiedermann's "Elektricität,"³ in a paper by de Hemptinne,⁴ and in the "Handbuch der Experimentalphysik."⁵

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³ Wiedermann, "Elektricität," Vol. 4B, Chapter 4, 1898.

⁴ De Hemptinne, *Z. physik. Chem.*, 12, 244-274 (1893).

⁵ "Die Elektrischen Eigenschaften der Flamme," by H. Becker, Vol. 13, 1929.

For some time attention was directed to the question whether ionization in the flame is of a chemical or thermal origin.⁶ The earlier investigations recognized that ionization could not result from chemical action alone, while Garner⁶ ascribes the ionization mainly to thermal origin on the basis of calculations using the Saha equation,⁷ which postulates a thermal equilibrium between atoms, ions and electrons. Haber,⁸ on the other hand, believes that the heat energy of an explosive reaction is not sufficient to account for the observed ionization currents. He suggests that ionization is brought about by collisions of the second kind between energy-rich products of the reaction and molecules possessing low ionization potentials. Although Haber's suggestion finds support in the spectroscopic detection of such groups as OH, CC and CH in flames, the origin of ionization in flames still remains open to further experimental investigation.

A number of attempts were made⁹ without success to arrest the propagation of a flame by means of an electric field. About the same time, Malinowski¹⁰ announced that he had arrested a 2.8% benzine (C_6H_{14})-air mixture in a transverse electric field. Later, Bernackyj and Retaniw¹¹ and Malinowski and Lawrow¹² found that not only the flame of a benzine-air mixture but also that of an acetylene-air mixture could be extinguished before it could pass through the condenser. In agreement with the experiments of Lind, no positive results were obtained with hydrogen-air mixtures. It is unfortunate that in the foregoing investigations no direct visual observations of the flame could be made while it was under the influence of the field. The gases were passed through the annular space between two metal cylinders between which a potential could be applied. The cooling effect of the wall must have been considerable in view of the small space (1.5 to 4 mm.) between the cylinders.

For some time we have been engaged in an investigation of the effects of an electric field on flames, and it is the purpose of this paper to explain briefly the method used and to make known some of the results obtained. In view of the fact that new equipment is being obtained for the production of steady high voltage, and for measuring voltage and ionization currents accurately, these results are preliminary in character.

⁶ Kirkby and Haselfoot, *Phil. Mag.*, [6] **8**, 471 (1904); de Muynck, *Acad. Roy. Belge*, 901 (1907); Garner and Saunders, *Trans. Faraday Soc.*, **22**, 281 (1926); Saunders, *ibid.*, **23**, 242, 256 (1927); Saunders and Sato, *ibid.*, **23**, 248 (1927).

⁷ Saha, *Phil. Mag.*, **40**, 478, 809 (1920); **41**, 267 (1921); **46**, 534 (1923); *Proc. Roy. Soc. (London)*, **A99**, 135 (1921).

⁸ F. Haber, *Sitzb. preuss. Akad. Wiss.*, No. 11, 162 (1929).

⁹ Lind, *J. Phys. Chem.*, **28**, 57 (1924) (H_2 and O_2); Wendt and Grimm, *Ind. Eng. Chem.*, **16**, 890 (1924) (C_2H_2 -air).

¹⁰ Malinowski, *J. chim. phys.*, **21**, 469 (1924).

¹¹ Bernackyj and Retaniw, *Ukv. Physik Abhand.*, Vol. II, No. 1, p. 9 (Dec., 1928).

¹² Malinowski and Lawrow, *Z. Physik*, **59**, 690 (1930).

Method

There are two ways in which an electric field may be applied: (1) longitudinally—that is, in the direction of the flow of gas; and (2) transversely—that is, across the gas stream. The longitudinal field method possesses certain advantages—namely, that the flame is not in contact with the electrodes and that possibly more information may be obtained concerning the role of ionized species by reversing the direction of the field. The first method was employed in these experiments.

Apparatus

To obtain a source of direct current, a transformer, synchronous rectifier, condensers and choke coil were arranged as in Fig. 1. The amount of

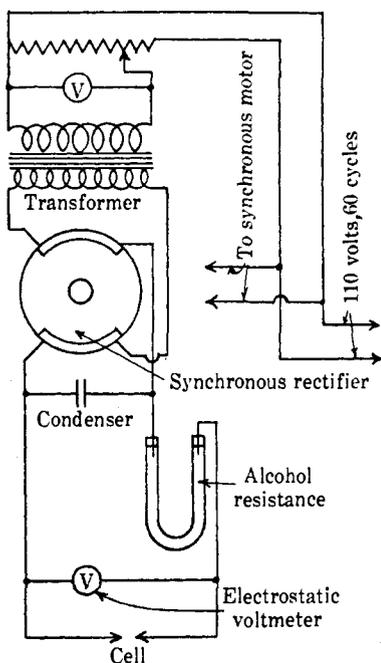


Fig. 1.—Apparatus used in experiments to determine the effect of electric field on flames.

ripples in the delivered potential was estimated to be about 5 to 8%. A synchronous rectifier is not entirely satisfactory because marked variations in potential sometimes occur; it served well, however, for these experiments. The potentials were measured by means of an electrostatic voltmeter. After considerable time had been spent on cell construction, a cell was finally adopted which was both durable and simple to construct. It consists (see Fig. 2) of a Pyrex glass tube of 1 cm. inside diameter into which two electrodes were placed 1 cm. apart. The electrodes consist of 80-mesh nichrome wire gauze bent by means of a special die into shape to fit the glass tube snugly. The outer edge of the electrodes was cemented to the glass tube by means of a porcelain cement, Insalute. The leads were attached firmly and brought out through side arms, in which they were sealed with wax. Ignition of the gas-air mix-

tures was accomplished by sparking (with a spark coil) across the electrodes. Of the gases used, methane, ethane, ethylene, propane, propylene, butane, isobutane and butylene were obtained reasonably pure in tanks. Pittsburgh natural gas was taken from the pipe line and carbon monoxide was prepared from sulfuric acid and formic acid.

Procedure

Air and the flammable gas were led separately through calibrated flow-

meters in amounts to give the desired mixture. They were passed into a mixing chamber and thence through the cell. Samples of the mixture were withdrawn and analyzed as a check on the flowmeters. The rate of flow of the mixture was adjusted to just balance the velocity of propagation of the flame in the opposite direction. Under these conditions a steady, stationary conical flame could be made to burn midway between the electrodes. The potential was then applied and increased and the effects were noted. Experiments were performed with the downstream electrode both positive and negative. A blast of air was used to prevent the glass cell from melting. The products of combustion were led to the open through a wide tube.

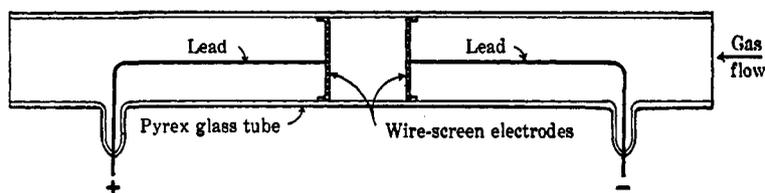


Fig. 2.—Diagram of cell used for confining a flame and applying an electric field.

Observations

The phenomenon observed, which is quite general for all the mixtures investigated, is that on application of the electric field the flame is invariably pulled toward that electrode which is negatively charged. Figure 3 shows this photographically. The upper picture is illustrative of a steady stationary flame of isobutane and air. The center picture shows the effect on the same flame on applying a field with the right-hand (upstream) electrode negatively charged. The lower picture shows the effect when the left-hand (downstream) electrode is negatively charged. This indicates that *the flame moves in the direction of positive ion flow*. It follows that the propagation of flame is *speeded up* if the upstream electrode is negatively charged and *slowed down* if the downstream electrode is negatively charged. Upon removing the electric field the flame returns to its original position in the tube.

If the potential applied is increased to a certain value, depending on the gas mixture, the flame may be extinguished. Depending on the direction of the field the phenomena observed are different. With the downstream electrode negatively charged, the flame is pulled toward this electrode as a body without much spreading. It undergoes intense oscillatory motions. Sometimes, when the potential is high enough, an occasional spark passes between the upstream (positive) electrode and the flame front. As the flame nears the negative electrode (with increasing potential) it becomes decidedly weak and unstable and then disappears. It is not possible to

decide whether the flame is pulled through the wire-gauze electrode through which it is unable to propagate, or whether it is extinguished near the electrode accompanying the removal of charged species. With the upstream electrode negatively charged, the flame having been drawn toward this electrode spreads out somewhat, undergoes vibrations and takes on a weak-like, fading-out appearance prior to its disappearance. Here there

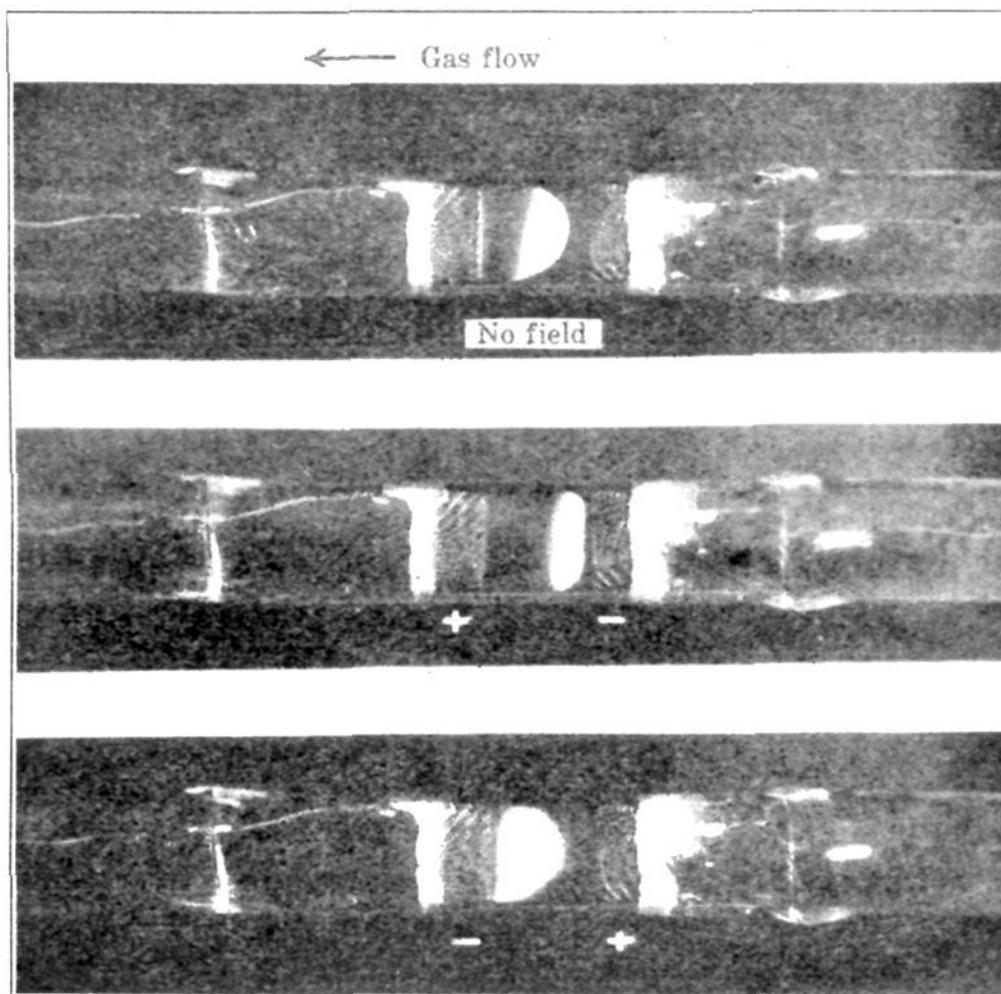


Fig. 3.—Photographs showing the effect of electric field on flames (natural size).

is no question that the extinguishing of the flame is in some way connected with the removal of charged species. For the sake of convenience we shall arbitrarily denote the field as negative when the downstream electrode is negatively charged, and as positive when the upstream electrode is negatively charged.

Table I summarizes the observations. Column 1 contains the flammable gas; column 2 the percentage of this gas mixed with air; column 3 the type of mixture—that is, whether it is richer or leaner in combustible gas than corresponds to a mixture in which gas and air are present in combining proportions. It should be noted that only in one or two cases was it

TABLE I
SUMMARY OF OBSERVATIONS

1 Combustible gas	2 Per cent. combustible	3 Type of mixture	4 Velocity of gases, cm./sec.	5 Voltage for extinguish- ing flame ^a	
				- Field	+ Field
Pittsburgh na- tural gas	9.96	Rich	38	7500	1000
	10.33	Rich	41	6800	1700
	10.59	Rich	41	4500	1800
	6.46	Lean	42	7700	..
	8.43	Lean	38	6000	..
CH ₄	11.61	Rich	29	9000	5000
	11.76	Rich	24	..	4300
	7.78	Lean	50	8000	..
C ₂ H ₆	8.07	Rich	23	6500	2000
	7.96	Rich	51	6000	..
	4.77	Lean	48	6300	..
C ₃ H ₈	4.90	Rich	39	5500	..
	2.97	Lean	31	7000	4250
	3.73	Lean	51	6500	4000
C ₄ H ₁₀	4.43	Rich	19	3400	..
	4.43	Rich	38	4800	..
	2.7	Lean	40	5300	1800
	2.76	Lean	47	5200	3000
Iso C ₄ H ₁₀	4.4	Rich	24	4300	..
	4.5	Rich	52	6000	..
	3.0	.. ^b	53	4800	1400
	2.5	Lean	34	7000	1400
C ₂ H ₄	10.74	Rich	28	1000	750
	10.8	Rich	51	5800	ca. 3000
	4.06	Lean	29.5	7700	ca. 2300
C ₃ H ₆	7.33	Rich	25	4500	..
	4.2	.. ^b	60	..	3600 ^c
	3.3	Lean	26	7500	5000
C ₄ H ₈	5.05	Rich	24	5000	..
	5.3	Rich	31	4300	..
	2.8	Lean	48	5000	ca. 1500
	3.0	Lean	ca. 50	6400	1600
CO	17.8	Lean	..	7000	.. ^d
	22.3	Lean	..	6500	.. ^d
C ₂ H ₂	3.87	Lean	..	7000	.. ^e

^a The potentials for negative fields are usually considerably higher than those for positive fields. This is due to the fact that with a negative field the upstream portion of the cell which is free of flame is also practically free of ions and therefore highly resistant. With a positive field the downstream portion of the cell is free of flame but contains ions carried along by the moving gases, rendering this space conductive.

^b Close to combining proportion mixture.

^c Very unsteady flame prior to application of voltage.

^d Flows too high to be measured.

^e Difficult to obtain steady flame with other mixtures.

possible to maintain a steady stationary flame between the electrodes with a mixture whose constituents were present in combining proportions. The flame of the latter mixture, which is close to one for which a maximum temperature and maximum flame speed are found, is usually extremely unsteady and very sensitive to small variations in composition.

Column 4 gives the velocity of flow of gases. These speeds may not correspond exactly to the horizontal speed of propagation of a flame in a 1-cm. tube measured in the usual way—namely, with stationary gases. Under the conditions of these experiments, turbulence is set up as a result of passage of the gases through the wire gauze. It becomes more pronounced with greater gas flows. Thus, it is possible to maintain stationary flames with quite different flows for the same percentage of combustible in the mixture.

Column 5 gives the potential at which the flame is extinguished with a negative field, and column 6 the potential at which the flame is extinguished with a positive field. Where dashes are indicated under positive field the flame was not extinguished with the highest voltage attainable (about 10,000 volts), although it was drawn toward the negative electrode, often violently, and set into intense vibration. At a somewhat lower voltage than this, sparks pass across the gap between one electrode and the flame. In a number of cases the flames were extinguished at voltages at which sparking occurred. However, this sparking was only intermittent (arising from gapping across the brushes of the synchronous rectifier). It was possible to observe that the flame was extinguished in a moment when the sparking ceased, in other words, when the applied potential was greatest. The voltages recorded were read just after the flame was extinguished.

Discussion of Observations

In many of the mixtures given in Table I the flame could be extinguished at practically every trial. In a few, the number of successful trials was from 7 to 8 out of 10. Where dashes are given under negative fields the flame could be extinguished only rarely, once or twice out of 10 trials. Dashes under positive fields, however, indicate no success in extinguishing the flame. Indeed, the phenomena are so easily reproducible that the experiment may be utilized for lecture demonstration with reasonable surety of success.

The results obtained by the longitudinal electric field method show:

1. The flames of rich mixtures of Pittsburgh natural gas (which is mainly CH_4 and C_2H_6), CH_4 and C_2H_6 are extinguished with positive fields; the flames of lean mixtures of these gases cannot be extinguished with positive fields.

2. The flames of lean mixtures of C_3H_8 , C_4H_{10} , iso- C_4H_{10} , C_3H_6 and C_4H_8 are extinguished with positive fields; the flames of rich mixtures of these gases cannot be extinguished with positive fields.

3. The flames of rich or lean mixtures of all these hydrocarbon gases and in addition CO and C_2H_2 , can be extinguished with negative fields. (It was found impossible to maintain a steady flame with rich mixtures of CO and C_2H_2 under these experimental conditions.)

The observed increase and decrease in the speed of propagation of flame may be linked with a greater or smaller concentration of ions. With a positive field in which an increase in velocity of flame propagation occurs, the ion concentration is greater than with a negative field in which a decrease in velocity is observed, because the field draws back into the flame ions which otherwise would have been carried downstream by the moving gases. An experiment by Malinowski¹³ lends support to this view. He found that the ionic current was greater in the faster than in the slower moving portions of an oscillating non-stationary flame. If ion concentration governs flame speed, then, because the latter is directly related to the temperature of a flame, it follows that the temperature of a flame should be markedly affected by an electric field.

Several important questions arise. (1) Is the function of the ions and electrons to activate unburned molecules in the fresh gases and so raise them to the reaction threshold? (2) Is the formation of ions and electrons a result of collisions of the second kind between highly energized products of the reaction and molecules possessing low-ionizing potentials in the Haber sense? (3) Is the removal of positive ions the only requisite for extinguishing a flame, or are active molecules clustered around them and also drawn away from the reaction zone? At the present time these questions cannot be answered satisfactorily. It is evident, however, in the light of these experiments, that the positive ion plays an important part in the maintenance of flames.

Knowledge of the current-voltage characteristics would throw much light on the nature of flame processes. This we hope to determine with new equipment which we are designing.

Mention should be made of some results by Thornton.¹³ He observed that while the flame of a 7% methane-air mixture (lean mixture) was speeded up in a transverse field, there was no effect on a 9.5% mixture (combining proportions). On the other hand, Malinowski and Lawrow¹² observed a marked slowing up of a 15% methane-air mixture (rich mixture). It has been shown above by the longitudinal field method that the flame can be speeded up or slowed down in a rich or lean mixture, depending merely on the direction of the field.

Some further experiments employing a transverse field may be mentioned. Using a duplicate of Thornton's cell it was found, in agreement with him, that with a 7% methane-air mixture the propagation of flame could be speeded up very much (2 to 3 times) if the flame was moving originally in

¹³ Thornton, *Phil. Mag.*, 9, 260 (1930).

the direction of oncoming unburned gases. If the velocity of the same mixture was adjusted so as to produce a stationary flame, the propagation was slowed down—that is, the flame moved in the direction of flow of gases. The strength of the field was below that which would extinguish the flame.

Likewise in rich mixtures, such as Malinowski used, propagation could be speeded up or slowed down under the same conditions mentioned above. Rich or lean butane-air mixtures showed the same effects. Acceleration of the flame was never observed, however, in a long rectangular cell two sides of which were of metal and two sides of transparent mica. In this cell, whatever the conditions, the speed of propagation was decreased by the transverse field.

These results clear up the apparent differences between the results of Thornton and Malinowski. The former worked with a flame in motion and the latter with an almost stationary flame or one moving slowly in the same direction as the gases. It is believed that these totally different effects are due to a difference in the shape of the flame fronts when the flame is in movement and when it is stationary,¹⁴ which probably results in the positive ions being drawn on the one hand more to the upstream side and on the other hand the downstream side of the flame front.

As the proof of this paper was being read, attention was drawn to a recent publication by Guénault and Wheeler.¹⁵ These authors show pictures of the distortion of flames under the influence of an electric field and reach the same conclusion as the writer—namely, that the flame moves in the direction of the positive ion flow.

Acknowledgment. The writer takes pleasure in acknowledging the assistance of Harold J. Muendel, coöperative research fellow, Carnegie Institute of Technology.

Summary

The effects of an electric field on the flames of ten hydrocarbon-air and carbon monoxide-air mixtures were investigated. The field was applied in the same direction as the moving gas between fine wire-gauze electrodes placed on either side of a stationary flame confined in a Pyrex glass tube. It is found that the flame is invariably pulled toward that electrode which is negatively charged. Photographs of this effect are shown. These indicate that the flame moves in the direction of positive ion flow, and it follows that the propagation of flame is speeded up or slowed down depending on the direction of the electric field. With appropriate field direction and strength, the flames of all the mixtures could be extinguished. The results show that:

¹⁴ See Mason and Wheeler, *J. Chem. Soc.*, 1227 (1920), and Thornton, Ref. 13.

¹⁵ Guénault and Wheeler, *J. Chem. Soc.*, 195 (1931).

1. The flames of rich mixtures of Pittsburgh natural gas, CH_4 and C_2H_6 , are extinguished when the upstream electrode is negatively charged; the flames of lean mixtures of these gases cannot be extinguished with this direction of the field.

2. The flames of lean mixtures of C_3H_8 , C_4H_{10} , iso- C_4H_{10} , C_3H_6 and C_4H_8 are extinguished when the upstream electrode is negatively charged; the flames of rich mixtures of these gases cannot be extinguished with this direction of the field.

3. The flames of rich or lean mixtures of all the above hydrocarbon gases and in addition lean mixtures of C_2H_2 and CO are extinguished when the downstream electrode is negatively charged.

4. Certain effects with a tranverse field are cleared up.

A brief discussion of the results is given. It is concluded that the positive ion plays an important role in the maintenance of flames.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS. II. THE VELOCITY OF SOUND IN SOLUTIONS OF CERTAIN ALKALI HALIDES AND THEIR COMPRESSIBILITIES

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RECEIVED JANUARY 29, 1931

PUBLISHED APRIL 6, 1931

In a previous paper² the velocities of sound in a number of organic liquids were reported. The measurements were made according to the method of Hubbard and Loomis,³ and from the data so obtained, with the aid of other data, the adiabatic compressibilities, and in some cases also the isothermal compressibilities, were calculated. For the details of the method reference must be made to the earlier papers. It shall suffice here to mention that the high frequency or supersonic waves were generated by the piezo action of a quartz disk. For producing the high frequency alternating field a common type of vacuum tube oscillator was employed, and the positions and separation of nodes were indicated by abrupt changes of frequency. A secondary quartz controlled oscillator served to fix the frequency at resonance, and using a double heterodyne method the position of nodes as read from a micrometer screw could be determined to within

¹ From the dissertation submitted by Egbert B. Freyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

² Freyer, Hubbard and Andrews, *THIS JOURNAL*, **51**, 759 (1929).

³ Hubbard and Loomis, *Phil. Mag.*, [7] **5**, 1177 (1928).