

THE EFFECT OF ULTRASONIC IRRADIATION ON ETHYL ALCOHOL -
" HYDROGEN PEROXIDE - WATER MIXTURES

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I. THE INTRODUCTION

The phenomenon of sound is defined as compressional waves capable of affecting the auditory nerve so as to produce the sensation of hearing. The range of audible compressional waves have frequencies between 20 and 20,000 cycles per second. This definition does not include compressional waves whose frequencies are so high as to be inaudible, and which are usually referred to as ultrasonic waves.

Sound then may be thought of in two ways -- objective and subjective. The former will include all compressional waves while the latter will include only those waves which will affect the auditory nerve and produce the sensation of hearing.

Various workers who have conducted experiments with ultrasonics have observed a whole series of chemical effects caused by acoustic waves of frequencies above the range of human audibility.

Oxidations promoted by ultrasonic radiations have been observed and several reactions have been studied. However, the mechanism of the oxidation is not yet clear.

The object of this investigation is to study the effect of ultrasonic irradiation on ethyl alcohol-hydrogen peroxide-water mixtures.

II. LITERATURE REVIEW

A. Introduction

For the general information and guidance of the reader in studying this work, it should be pointed out at the offset that he will encounter conflicting statements and hypotheses in the literature review. It appears that some work in the field of ultrasonics is somewhat in keeping with a statement ⁽⁷⁹⁾ made by the late Professor Michelson, once head of the University of Chicago Physics Department, who said "try any fool thing. It may not be as foolish as it seems. You may discover something." Professor Michelson did not follow his own advice, but held to the philosophy "that the future truths of Physical Science are to be looked for in the sixth place of decimals."

It is not improbable that the advance of science would be more rapid and thorough if there were more scientists following Michelson's example in diligently seeking accurate quantitative relationships rather than theorizing on scanty and perhaps doubtful data. Theory guides -- but the experiment decides.

In composing the literature review for this investigation, many ramifications of the field of ultrasonics that remotely concern this work are included -- primarily due to the newness of this field of study and the lack of an understanding of certain phenomena. In the section discussing the effects of ultrasonic energy, many subjects

have been only enumerated. This is done with two thoughts in mind - firstly, to acquaint the reader with the possibilities in this relatively new field of research; and secondly, an attempt to stimulate an interest for further research in this field of study by those in whose hands this work may fall. It is conceded that all of the literature published has not been considered. However, no author was intentionally neglected, but due to financial limitations and the difficulty in which these publications could have been made available, it was impracticable to include them.

In order to have a clearer understanding of sound phenomena, it is strongly urged that the following definitions, concepts, and relations of sound phenomena be kept in mind while considering this work which utilises a "special" type of sound wave.

B. Definitions, Concepts, And Relations Of Sound Phenomena

Wave Motion. A wave is a temporary change or condition of a medium, which moves through the medium and transmits energy outward from the source (166). The study of wave motion is often properly referred to as the study of dynamics of elasticity. The deformation may be a single pulse or it may consist of a succession of periodic disturbances. The former is referred to as a wave pulse; the latter as a wave train (10).

Characteristics Of All Wave Motion. The characteristics of all wave motion are:

(a) The motion of the medium is vibratory. Different parts of the medium vibrate successively -- each back and forth about its own equilibrium position (10).

(b) Only the wave form or the disturbance -- not the medium -- travels. In other words only energy is propagated (10,166).

Types Of Waves. Waves are classified on the basis of how the particles of the medium move with reference to the direction of propagation of the wave form (166).

(a) Transverse Wave. A transverse wave is one in which the particles of the medium vibrate, or the condition of the medium changes, at right angles to the direction of propagation of the wave (167). Light and radio waves are transverse waves of this type (11).

(b) Longitudinal Or Compressional Wave. A longitudinal or compressional wave is one in which the particles of the medium vibrate, or the condition of the medium changes in the direction of propagation of the wave (168). They result from deformation due to tensions and compressions. Such waves can be propagated through air, and when capable of exciting the auditory nerve, they are called sound waves (11).

(c) Other Types. There are other types (11,168) which are not of immediate concern and will not be considered beyond enumerating. They include: gravitational, torsional, plane, circular, spherical, ellipsoidal, etc.

Fundamental Wave Concepts. In the consideration of wave trains certain concepts and relations are fundamentally important (11).

(a) Wave Length (λ). For any wave train, the distance (along the direction of propagation) between two successive corresponding points on the wave train is called the wave length (11). This may be thought of as the distance from crest to crest or from trough to trough for a transverse wave, or from compression to compression, or from rarefaction to rarefaction for a compressional wave.

(b) Frequency (n). The frequency of a wave motion is the number of complete waves which pass a given point per second (12). The medium makes one vibration for each wave that passes -- hence the frequency of a wave motion has precisely the same significance as the frequency of periodic motion.

(c) Period (T). The period of a wave motion is the time required for a complete wave to pass a given point, or the time required for one complete vibration of the medium. It is the reciprocal of frequency (12).

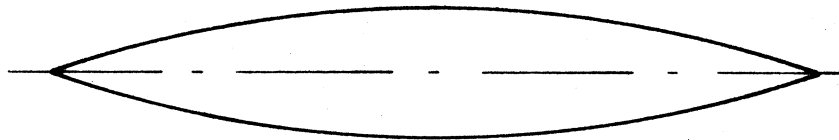
(d) Velocity (v). The velocity of the wave motion, which is the velocity with which the disturbance spreads, is related to the frequency and wave length in the fundamental manner such that $v = n \lambda = \lambda/T$ (12).

(e) Harmonic Motion. Harmonic motion is a vibratory motion in which the moving object sweeps back and forth repeatedly over the same path. In harmonic motion "the acceleration of the vibrating body and the restoring force acting upon it are proportional to its displacement from the midpoint of its path, and are directed toward that point" (102).

(f) Harmonic Waves. When waves are propagated from a source vibrating with harmonic motion the waves emitted are called harmonic waves (12). When simple harmonic waves are plotted against time on a graph, the sine or cosine curve results.

(g) Fundamental Tones, Overtones, And Harmonics. "The fundamental tone is produced when a body is vibrating in the smallest number of parts. Overtones are produced when a body is vibrating in any number of parts greater than the number required for the fundamental tone" (79,103). Figure 1 depicts a graphic illustration of the fundamental tone, overtones, and harmonics.

(h) Amplitude (r). The amplitude of a wave is the maximum distance that a particle of the medium vibrates to either side of its equilibrium position (169).



*Fundamental Tone Or
First Harmonic*

Frequency n



*First Overtone Or
Second Harmonic*

Frequency $2n$



*Second Overtone Or
Third Harmonic*

Frequency $3n$



*Fifth Overtone Or
Sixth Harmonic*

Frequency $6n$

Figure 1

Harmonic Vibrations of a String

Foley, A.L. "College Physics." p. 578. P. Blakiston's
Son & Co., Inc., Philadelphia. 1937. 3d ed.

Hausmann, E. and P. E. Slack. "College Physics." p. 550.
D. Van Nostrand Co., Inc., New York. 1939. 2d ed.

(i) Phase. The phase of a particle participating in a wave motion is the fraction of a period that has elapsed since the particle last passed through its position of equilibrium. Phase may be expressed in time or in an angle which is proportional to time.

(j) Pitch. The pitch of a tone "is directly proportional to the number of condensations and rarefactions received per second, which in turn is determined by the vibration frequency of the sounding source" (104).

(k) Intensity Of Sound. Intensity of sound "is the time rate of transfer of vibratory energy per unit of sectional area of the sound waves" (104).

C. Classification And Conclusions Regarding Sound Waves And The Media Through Which They Are Propagated

Classification Of Sound Waves. In the effect upon the ear, sound may differ in three respects only -- pitch, loudness, and quality (81). However, acoustical vibrations are divided into three classes based on the physiological process of hearing (204). In the first class we have the so-called sub-audible sounds of such low vibration frequency that we cannot assign any definite pitch. If the air column in an organ pipe makes less than about 30 vibrations a second, the human ear perceives the separate pulses of the air as a fluttering sound.

The second class is known as the audible or hearing range with frequencies from about 30 to 20,000 vibrations per second. Above 20,000 vibrations per second is the third class known as the super-sonic or ultrasonic range. These ultrasonic vibrations produce no sensation of hearing, but cause phenomena not caused by sound vibrations to which the ear is accustomed.

It is somewhat interesting to note that the human eye has limitations similar to the limitations of the human ear. Infra-red and ultra-violet light cannot be seen, though photographs can be taken by their aid in a room which appears to be dark.

Conclusion Regarding Sound Waves And Media Through Which They Are Propagated (30)

. Wave propagation is accomplished by the transmission of vibratory motion from particle to particle of the medium in which the wave is traveling. The medium as a whole does not move nor is any part of it permanently displaced when a wave passes through it. In a perfectly elastic medium the force of restitution is proportional to the displacement (Hooke's Law); if left to itself after displacement, a particle in such a medium executes simple harmonic motion.

A wave cannot pass through an inelastic medium since there is no force of restitution. Elasticity is a necessary property for transmission entirely inside a medium, and since fluids (liquids and gases) have but one kind of elasticity (volume elasticity), compressional waves are the only kind that fluids will transmit.

Sound waves must be compressional waves (another name for longitudinal waves), since sound waves are transmitted by fluids as well as by solids. As long as the medium is homogeneous and isotropic, there is at no time any tendency for a wave or any part of the wave energy to move backward. In such media, waves continue to move in the direction in which they start.

Whenever and wherever there is a change in the elasticity or density of a medium in which a wave is traveling, a part of the energy of the wave is reflected and part refracted; usually with a change in direction and frequency with absorption and dissipation of energy.

D. History Of Ultrasonics

One of the earliest investigations of the highest pitch which could be recognized was done by Despretz ⁽⁶³⁾ in 1645. The upper limit of 30,000 vibrations per second was said to have been reached. This was judged, not by actual measurement of the frequency, but by estimates made by musicians with trained ears who claimed to be able to recognize the number of octaves which they could follow into the regions of high frequency vibrations.

Galton ^(91,120), in 1833, designed a whistle for the production of sounds near or beyond the upper limit of human audition. This whistle, known as the "Galton Pipe," was for many years the accepted apparatus used by physicians for testing the ear in respect to its

ability to recognize high pitch sounds. Frequencies of 25,000 vibrations per second were obtained with this instrument.

In 1874, Koenig ⁽¹¹⁴⁾ considered the results of Despretz wholly unreliable. Koenig constructed tuning forks, steel bars, high pitch organ pipes and vibrating plates which he brought to America and exhibited at the Philadelphia Exposition in 1876. He made a study of the upper limit of audible sound with short cylindrical bars which could be made to produce longitudinal or transverse vibrations by striking them with a hammer.

Various investigators studied the upper limit of audible sound both before and after Koenig's initial work, but their studies resulted only in disagreements and controversies. They found the upper limits in the audible range varying from 20,000 to 50,000 vibrations per second.

In 1899, Koenig ⁽¹¹⁴⁾ studied the region above audible sound by means of tuning forks of a few millimeters in length. He produced frequencies as high as 90,000 and is regarded to be the first to make a real study of ultrasonics. The frequencies were determined by Kundt's method of "dust figures" in which the sound is caused to enter a glass tube containing lycopodium powder which arranges itself in wave patterns.

Edelmann ⁽⁶⁸⁾, in 1900, constructed an improved form of the Galton Pipe which gave a greater sound energy than the earlier instrument. He claimed that certain individuals could hear a tone of

50,000 vibrations per second while frequencies as high as 110,000 could be recorded by the Kundt dust figures.

In 1907, Altberg ⁽¹⁾ investigated the ultrasonic waves emitted by the spark discharge of a condenser. These electrical discharges are oscillatory. That is, the flash and crack of what appears to be a single spark to the eye and ear, is in reality a very rapid succession of sparks. Each of the elementary sparks gives out a single acoustic air pulse, and the collection of these pulses forms a wave train whose wave length can be measured. Altberg found wave-lengths as small as 1 millimeter (332,400 vibrations per second) or an octave above any previously recorded sound.

The next period of investigation was during World War I when ultrasonic apparatus was brought from the laboratory and developed on an engineering scale for military purposes. In 1917, Langevin ⁽¹¹⁹⁾ utilized the phenomenon of piezoelectricity, discovered by the Curie brothers ^(42,60) in 1880, for the production of high frequency sound waves under water for the detection of submarines by the echo returned from the submerged hull of the vessel. Langevin was probably the first to recognize and show the enormous increase in the amplitude of the vibrations of the quartz plate, when the electrical frequency is tuned to agree with its natural mechanical frequency.

Since the first World War, detached groups and individuals are testing the potentialities of ultrasonics in widely separated laboratories. However, the literature of the subject is meager and dated, and there is little exchange of current information.

B. Types Of Ultrasonic Generators

Interest in the effects and possible applications of intense ultrasonic waves has centered mainly on their propagation in liquid systems. Until recently this has had the influence of directing attention and interest to methods of generation of ultrasonic waves in liquid rather than gaseous systems.

In general, there are three types of sound generators in commercial use. These are the piezoelectric oscillator and the magnetostriction oscillator which use electrical energy as a source of power. These oscillators have the common feature that they were rendered practicable only by the advances in the technique of high frequency electric oscillations made possible by the use of large electron tubes. The third generator is the siren type unit which uses compressed air as a source of power.

The Piezoelectric Oscillator. This type has been most useful for the generation of the highest frequency oscillations (94). It consists essentially of a piezoelectric crystal, generally of quartz, cut so that the application of a high frequency voltage to the two crystal faces causes resonant mechanical oscillations, arising from the changes of dimensions of the crystal. The frequency of the electrical oscillations is controlled by the natural frequency of the quartz. In general, the crystal is submerged in a bath of insulating oil which then forms the transmission medium for the mechanical oscillations and enables the irradiation to be applied

to systems under study. The piezoelectric method is generally used in the range of 100 kilocycles per second and above.

The Magnetostriction Oscillator. This type has been most generally applied to the production of oscillations of high audible and low ultrasonic frequencies (94). It consists of an oscillating element of nickel, which exhibits the phenomenon of magnetostriction in a very regular manner -- this phenomenon being the change of physical dimensions with intensity of magnetization. In the usual design of an oscillator, the nickel forms the core of the inductive element of a tuned circuit in which oscillations of resonant frequency are sustained by an electronic circuit. The presence of the mass of metal in the oscillating magnetic field, and the necessity of keeping the length of the nickel rod adequate for complete magnetization cause difficulties to arise when this method is used for very high frequencies, and in general it is most useful in the range from 5,000 to 20,000 cycles per second.

Siren Type Generator. The newest sound generator is the siren type (151). The generator is essentially a high speed air siren driven by a variable speed air turbine. Compressed air passes into a rotating hollow disk, then radially outward through slots on the periphery past stationary vanes which cut it into short pulses. The pulsations or vibrations are focused by horns in the stator to a reflector which further directs the vibrations as required by the application. Frequency of the sound waves is determined by the speed of rotation. Intensity is determined by the amount of air forced

through the generator. With this type of generator both frequency and intensity are easily varied. The standard unit operates over a frequency of 1,000 to 200,000 cycles per second with intensities from about 100 to 170 decibels. From 50 to 70 per cent of the energy in the compressed air is converted to sound energy.

In this investigation only the piezoelectric oscillator will be employed.

F. The Piezoelectric Effect

Discovery. In 1880, Pierre and Jacques Curie (42,60) discovered that particular crystals showed positive and negative charges on certain portions of their surface when compressed in predetermined directions. In order to observe this effect the Curie brothers prepared flat plates from crystals cut according to the proper crystal orientation. The cut plates were then fitted with tin-foil as electrodes and connected to an electrometer. Pressure was applied and released in given directions. It was found that the charges were proportional to the pressure and disappeared when the pressure was released.

Definition Of Piezoelectricity. This method of producing electrical charges was later termed "piezoelectricity" by Harkel (42). Cady (42) defines piezoelectricity as "electric polarization produced by mechanical strain in crystals belonging to certain classes, and the polarization being proportional to the strain and changing sign with it."

Crystals Exhibiting Piezoelectric Properties. Later investigations (93,105) have shown that this effect appears in many other crystals of varied crystal systems and is not confined to certain types of crystals. Electrical deflections were observed on the application of pressure to plates from the following crystals: zinc blende, sodium chlorate, boracite, tourmaline, quartz, calamine, topaz, tartaric acid, cane sugar, and rochelle salt. The common property possessed by all crystals so far found to be piezoelectric is the presence of one or more polar axes, or an absence of symmetry.

Polar Axis. A polar axis in crystallography is defined as an imaginary direction through the crystal in which the two sides or ends of the crystal cannot be interchanged. In other words, if the crystal is turned 180° about the imaginary direction line, it cannot be made to coincide with its original position. This point is made clearer by considering figure 2. This is a diagram (18,20,43) of a crystal of quartz which is most used for piezoelectric purposes. The crystal belongs to the trigonal system (three axes equally inclined, not at right angles, and all equal) and has three twofold polar axes which are indicated by X_1 , X_2 , and X_3 . In every case these axes connect two dissimilar opposite edges of the six-sided prism. This can be seen by the edges of the small faces marked a and b, which are missing on the opposite side. The fourth axis, Z, is threefold and not polar because by turning the crystal through 180° about one of the three X-axes, one side of the crystal may be made to coincide with its initial position.

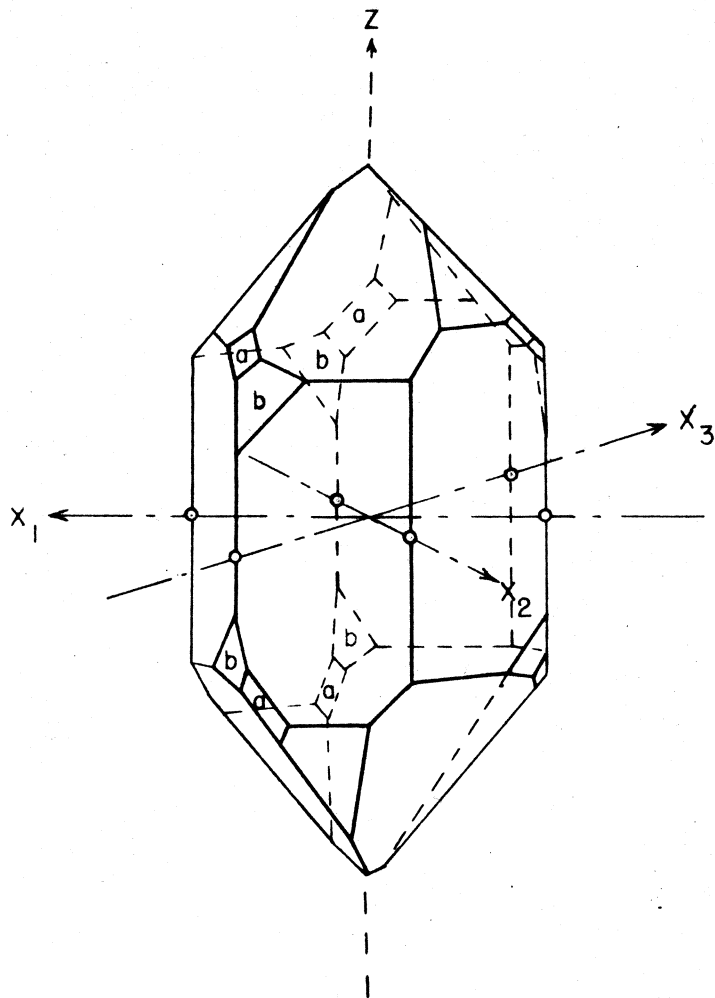


Figure 2
Quartz Crystal

Bergmann, L. and H. S. Hatfield. "Ultrasonics." p. 12.
John Wiley and Sons, Inc., New York. 1946.

Axis of Symmetry. An axis of symmetry is an imaginary line about which a crystal may be rotated so that it presents exactly the same appearance more than once in the course of a complete revolution. If the self-coincidence occurs twice, that is, the original position is repeated as a result of rotation through 180° , the axis is said to be one of twofold ⁽³⁵⁾ symmetry or a diad axis.

Optical Axis. The Z-axis is defined as the optical axis because it is an axis of optical symmetry. The polar axes are determined not only from the external form of the crystal but also by the fact that their two ends are quite different in physical and chemical respects. Bergmann ⁽¹⁸⁾ states that the patterns produced by etching, and the rate at which etching takes place are different at the ends of a polar axis. If mechanical pressure or tension is applied to the crystal, opposite electric charges appear at the ends of a polar axis, or on surfaces at right angles to it. To produce the electric charges, mechanical stress need not be applied in the direction of the polar axis as one component of the stress in the direction of the axis will produce the same effect.

Crystal Cutting. The portions of a quartz crystal used in piezoelectricity are cut as far as possible in such a way that one pair of surfaces are at right angles to the polar axis -- sometimes called the piezo-axis. The reason for cutting crystals in this manner is that the maximum charges produced by mechanical stress only appear at the ends of a polar axis. This phenomenon will be discussed more fully later on.

Piezoelectric Effect. Figure 3 shows the phantom position of a rectangular and cylindrical plate to be cut from a quartz crystal. In the rectangular plate the edge d is parallel to the polar X-axis, the edge b parallel to the optical Z-axis, and the length l parallel to the third coordinate axis Y.

In figure 4, a cut quartz plate with the directions of the axes shown, illustrates the following effects:

- (a) Pressure applied in the direction of the X-axis charges the surface bl and opposite to it, normal to the X-axis, positively or negatively respectively. This is known as the longitudinal direct piezoelectric effect.
- (b) A tension applied in the direction of the Y-axis charges the surface bl and that opposite to it in the same way positively and negatively respectively. This is known as the transverse direct piezoelectric effect.
- (c) Tension applied in case 1 and pressure applied in case 2 produce electric charges of opposite sign on the surfaces bl.
- (d) Pressure or tension applied in the direction of the Z-axis gives no piezoelectric effect.

In 1881, Lippman (45,124,145) predicted the reciprocal piezoelectric effect by calculations. In the same year the Curies (124) had verified Lippman's prediction and showed that the piezoelectric coefficient of quartz had the same value for the converse as for the direct effect. This converse or reciprocal effect is such that if a properly cut quartz crystal is brought into an electric field

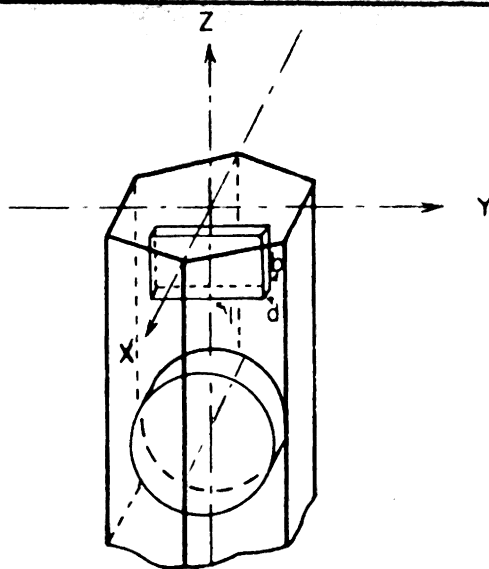


Figure 3

Phantom View of Quartz Crystal

Bergmann, L. and H. S. Hatfield. "Ultrasonics." p. 13.
 John Wiley and Sons, Inc., New York. 1946.

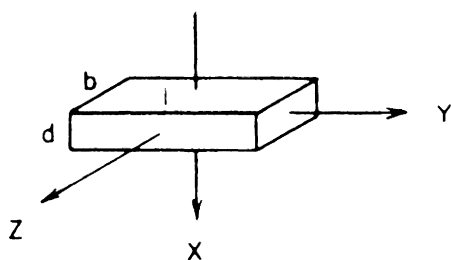


Figure 4

Cut Quartz Plate

Bergmann, L. and H. S. Hatfield. "Ultrasonics." p. 13.
 John Wiley and Sons, Inc., New York. 1946.

of force so that the direction of the field is the same as the direction of the piezoelectric axis, the crystal is made to contract or expand in certain directions.

Again referring to figure 4, the reciprocal piezoelectric effect may be described as follows:

(a) With a positive charge on the surface bl and a negative charge on the opposite surface, the crystal expands in the direction of the X-axis. This is known as the longitudinal reciprocal piezoelectric effect.

(b) With a positive charge on the surface bl and a negative charge on the opposite surface, the crystal is compressed in the direction of the Y-axis. This is known as the transverse reciprocal piezoelectric effect.

The reversal of the electric charge changes expansion into contraction and vice versa.

G. Piezoelectric Phenomena From Point Of View Of Molecular Theory

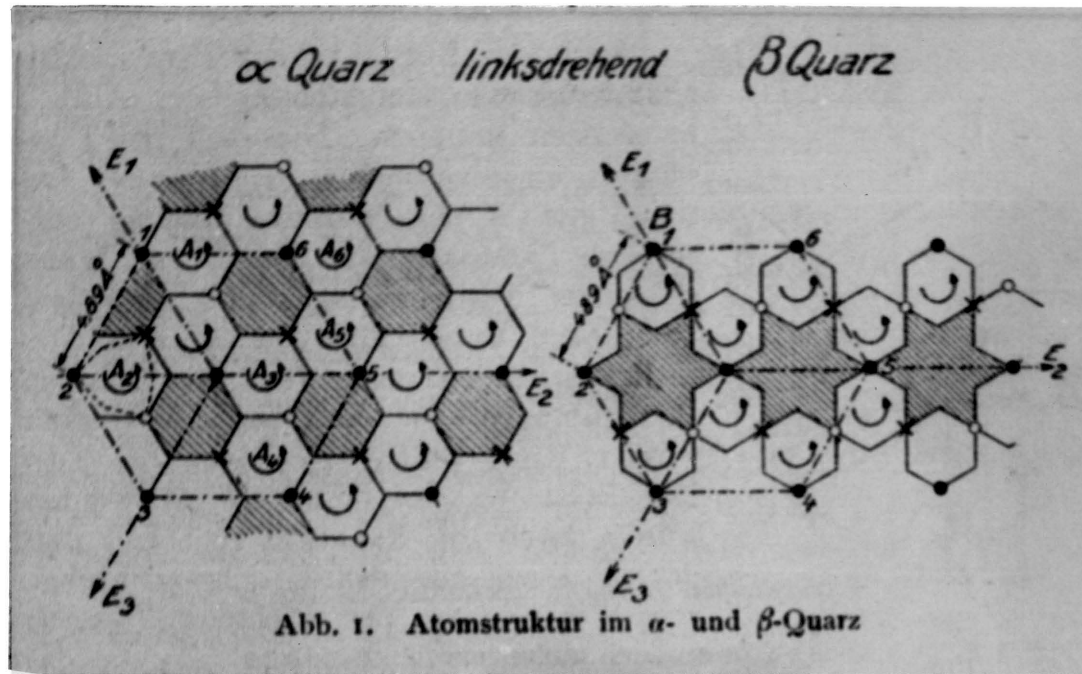
Meissner (133) offers an explanation for the piezoelectric phenomena. He states that it is known for a quartz crystal plate arranged with the molecules in a left or right handed direction that it is also optically left or right turning. This information is obtained by chilling the quartz crystal in the charged condition so as to determine the orientation of the electrical axis.

Structural Cell. Reference must be made to a structural cell for the classification of the charge obtained upon placing an atom

along the axis of a structural cell. By a structural cell is meant the arrangement of the atoms in the three structural planes about an axis. Figure 5a gives the projection of these atoms about the different axis systems lying beside it (A_1, A_2, A_3 , etc). Symbols used in figure 5a are as follows:

- are the silicon atoms of the first plane.
- are the silicon atoms of the second plane.
- × are the silicon atoms of the third plane.

Between each of the silicon atoms lies an oxygen atom and all the atoms lie in a helix about the axis. With the right hand crystal the helix is to the right -- with the left hand crystal it is to the left. There is no complete helix existing about the cross-hatched hexagons since the oxygen atoms are here arranged differently than about the axis. According to the work of Bragg and Gibbs (36,92) using X-rays, the oxygen atoms do not lie at the corners of a hexagon, but are displaced toward the center. Considering this displacement and using the value of the atomic diameter ($\phi_{Si} = 1.87 \text{ \AA}$ and $\phi_O = 1.3 \text{ \AA}$), one obtains the model arrangement of atoms shown in figure 6 and the projection of the atomic structure in the three planes according to figure 7. Figure 7 corresponds to the projection of the atomic structure of the three planes -- to the left the atomic cell and to the right the plane corresponding to figure 5. The atoms of the different planes are marked 1, 2, 3, etc. In a model constructed according to figure 7, one can



a.

b.

Figure 5

Atomic Structure in α - and β -Quartz

Meissner, A. Über piezo-elektrische Kristalle bei Hochfrequenz. Z. techn. Phys. 8, 75 (1927)

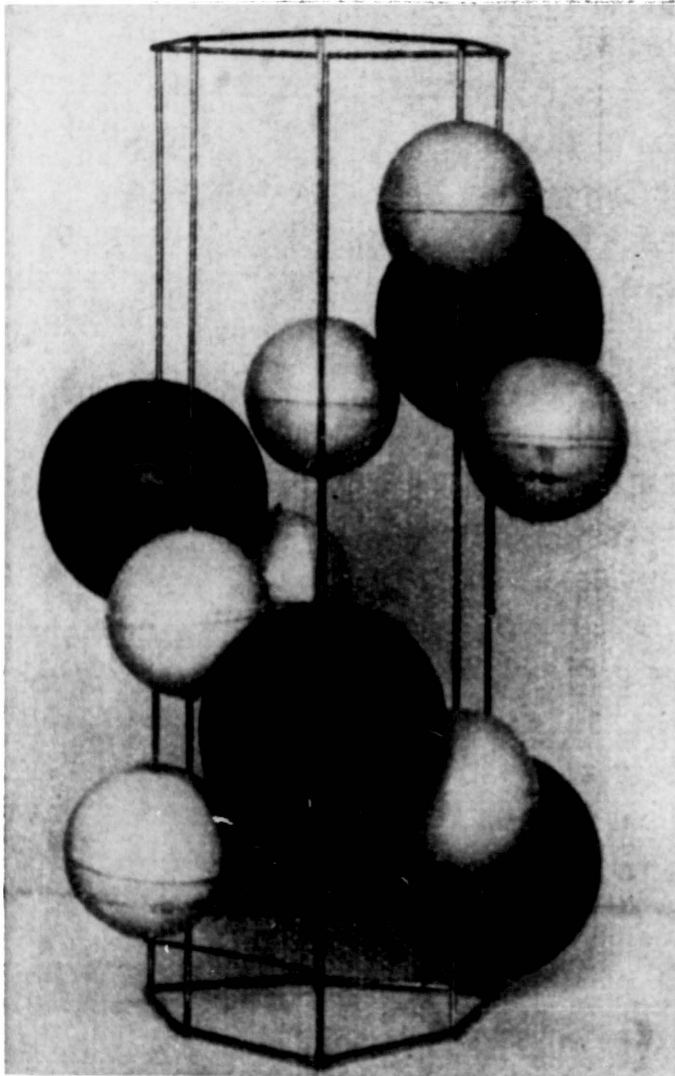


Figure 6

Model of Structural Cell

Meissner, A. ^{••}Über piezo-elektrische Kristalle bei Hoch-
frequenz. Z. techn. Phys. 8, 75 (1927).

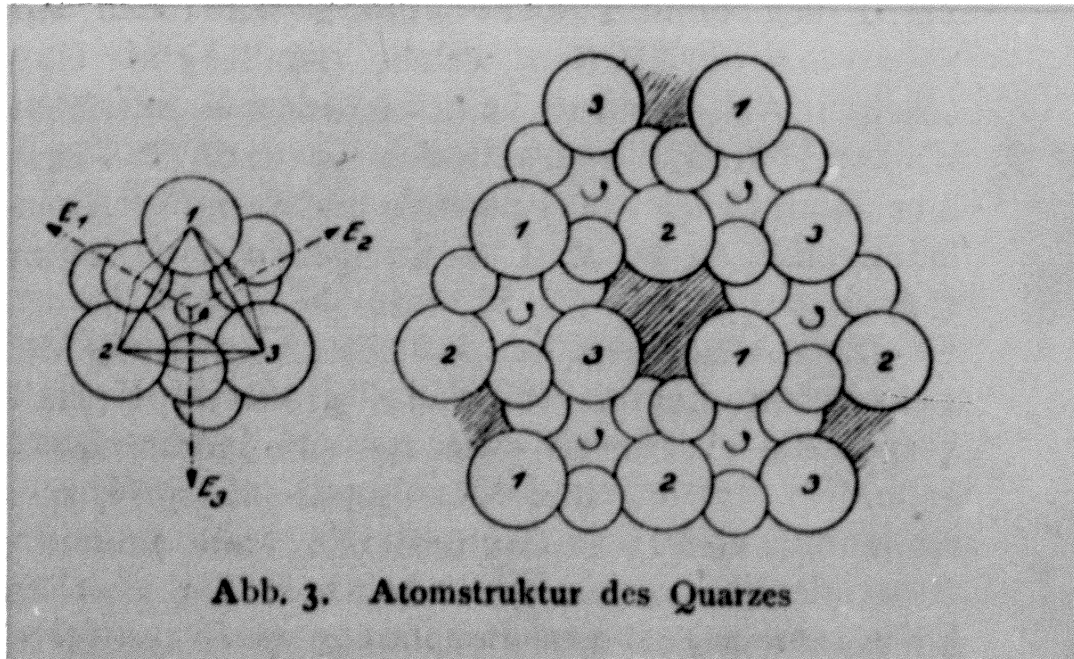


Abb. 3. Atomstruktur des Quarzes

Figure 7

Atomic Structure of Quartz

Meissner, A. Über piezo-elektrische Kristalle bei Hochfrequenz. Z. techn. Phys. 8, 75 (1927)

very readily see these six silicon atom planes which give the main and the first secondary waves. It is necessary in constructing the model to reduce the diameter of the atoms. According to this model, one could assume that the rotation of a light beam could be affected by the silicon atoms alone, since the planes of the light rays passing through the cross-hatched areas are also rotated. In these cross-hatched areas only the silicon atoms are in a special arrangement and not the oxygen atoms. The rotation through one cell (three silicon atoms, $h = 5.375 \times 10^{-7}$ mm) amounts to $\lambda = 760 \times 10^{-7}$ mm $\times 12.66^\circ / 1.87 \times 10^{-6} = 6.8 \times 10^{-6}$ degrees. The low value of rotation could find an explanation according to Lindemann (123) in that the wave of the light passing through is over 1000 times larger than the characteristic vibration of the silicon atoms ($\beta = 1.87 \times 10^{-7}$ mm).

According to Bragg each silicon atom has four positive charges and each oxygen atom has two negative charges. For a simplification one refers to the hexagon projection shown in figure 8c. (The subsequent discussion may be considered valid for the crushed hexagon projection shown in figure 8b. One needs only to be careful that two oxygen atoms always lie superimposed above each other when drawing the atoms of the three planes above each other. Now each of the oxygen atoms carry four equal negative charges. In figure 8 all atoms are marked with the appropriate charges.)

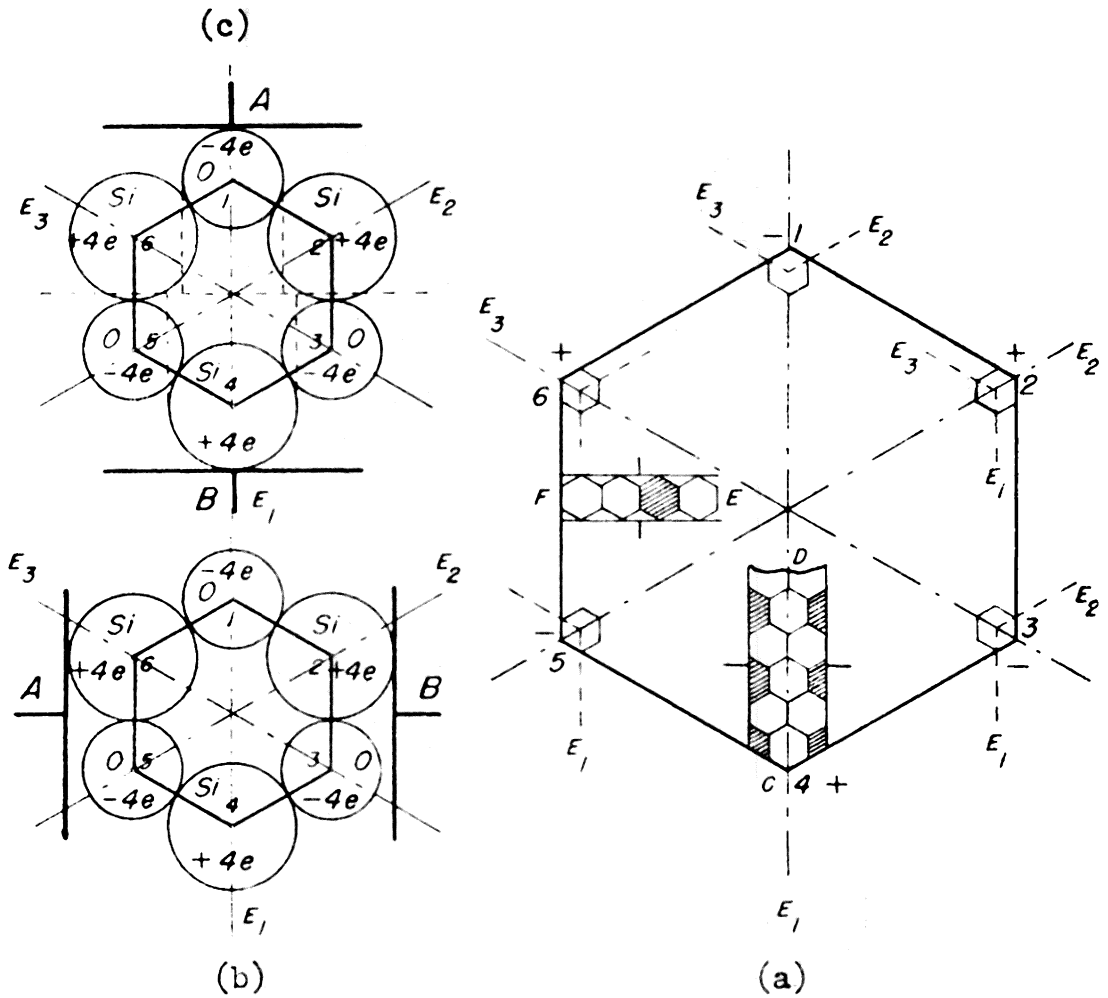


Figure 3

Illustration of Piezoelectricity

Meissner, A. Über piezo-elektrische Kristalle bei Hochfrequenz. Z. techn. Phys. 8, 76 (1927).

It is assumed that in the unexcited and rest position, all the lines of force of the silicon and oxygen atoms are mutually bound. In the equilibrium position one has to deal with a system of fixed, balanced electrical dipoles to some extent. Externally there is no charge.

Piezoelectric Effect. If pressure is applied on the corners 1 and 4 with the electrodes A and B in the direction of the electrical axis, the oxygen and silicon atoms at corners 1 and 4 are slightly displaced towards the center and the electrical balance is disturbed. The reaction of O_1 upon electrode A is that O_1 moves down and electrode A touches Si_1 and Si_2 . Now both positive charges of Si_1 and Si_2 have an influence upon A ($\sqrt{3}e - 4e$), and on electrode B the negative charges of O_3 and O_5 take effect ($-3e \neq 4e$). Therefore, electrode A becomes negative electrically and electrode B positive electrically. If pressure is applied on corners 2 and 5 these will show the opposite polarity of corners 1 and 4. By pressing on corners 3 and 6, one gets the same polarity as corners 1 and 4.

By pulling in direction A and B, atoms O_1 and Si_4 are displaced from the equilibrium towards the outside. Thereby the influence of both Si_2 and Si_6 upon A is weakened and the influence of the negative O_1 upon A becomes stronger. Electrode A now becomes electrically positive and electrode B under the influence

of positive Si_4 becomes electrically negative. The same holds true for the other corners and pulling produces exactly the opposite polarity from pushing at all corners.

Figure 8b shows that either pushing or pulling on the side surfaces of the hexagon which are parallel to an electrical axis cannot result in a formation of electrical charges. In this case A and B always have the influence of the same number of positive and negative atomic charges. $\nearrow Si_6$ and $- O_5$ give an influence on A equivalent to O_1 , and likewise $\nearrow Si_2$ and $- O_3$ give some influence on B.

It is assumed that the orientation of the electrical axis in a large crystal is the same as that on the atomic hexagon and also that the large crystal has definite electrical axes. If these assumptions are true, then the conclusions from the atomic hexagon can be applied to large crystals. A large crystal is shown in figure 8a. It may be seen that the corners 1, 2, 3, etc. become alternately positive and negative under pressure exactly as with the atomic hexagon. If a plate is cut from a large crystal parallel to the electrical axis CD, one obtains no charges on the atomic hexagon and therefore none on the plate. A plate cut perpendicular to the electrical axis EF, gives charges with pressure or tension. Pressure upon all corners at the same time can give rise to no charges since all atoms will displace themselves equally and the orientation of the atoms with respect to themselves will remain the same and the equilibrium is not disturbed.

Pyroelectricity Compared With Piezoelectricity. The source of pyroelectricity can also be explained by the atomic hexagon (figure 8c). An increase in temperature should give A a positive charge and B a negative charge. This is equivalent to tension. Once equilibrium temperature is reached, A and B should no longer have a charge.

From previous considerations it was seen that in the case of piezoelectricity, electrode B became negative electrically under tension and this was explained by the fact that the silicon atoms were displaced more than the oxygen atoms from the equilibrium position in the direction B. Since B becomes negative with a temperature change this must also be a case of unequal displacement of the atoms. This can only be brought about if the action of the temperature change is different on a silicon atom than on an oxygen atom.

It must be assumed that the silicon atom receives heat faster than the oxygen atom. In this way the silicon atom expands before the oxygen atom and is displaced in the direction of the axis before the oxygen atom. It is not expected that the oxygen and silicon atoms should charge equally, since all the thermal constants of the two elements are different. Under the influence of the unequal heat absorption, electrode B comes more under the influence of the four positive charges of Si_4 and so becomes electrically negative.

The fact that electrode A becomes positive can be explained with the assumption that the displacement of the silicon atoms

from equilibrium is less than twice the displacement of the oxygen atoms. The displacement of O_1 to the outside is therefore greater than the components of the displacement of Si_1 and Si_2 in the direction of electrode A. Electrode A thereby comes under the influence of the four negative charges and becomes positive.

The disappearing of the charge at the final temperature conditions could be explained by the fact that the oxygen and silicon atoms have again assumed the same relative positions as at the beginning. Therefore, all atoms continue to move or adjust themselves until they are once more in electrical equilibrium. Upon cooling, the opposite electrical effects take place.

Figure 5b is a β - quartz structure. Upon raising the temperature over $575^\circ C$ the atoms change from the α - state to the β - state. The atoms find a more stable position with smaller distances from the axes than in the α - state and by larger empty spaces between the axes. As the structural picture shows, plates cut perpendicular to the electrical axis in this plate can show no piezoelectric effect. In this way one could explain without trouble both the pyro and piezoelectric effect in quartz. These explanations seem to substantiate all the assumptions made regarding the displacement of the atom layers. Since all of these explanations have been made as a direct consequence of the assumptions, it seems that an examination of the piezoelectric effect and electrical acoustic exciting methods could be a way of determining atomic arrangements.

H. Effect Of Quartz Crystal Vibration

Position Of Crystal Plate And Electrodes. Assume a properly cut quartz crystal plate placed between two metallic electrodes in such a manner (figure 9) that the piezoelectric axis or polar axis of the quartz plate is perpendicular to the electrodes.

Crystal Oscillations. If the two electrodes which are in contact with the quartz plate are connected to a source of alternating current, the plate will be compressed in one-half of the alternating cycle and expanded by the same amount on the other half of the alternating cycle. The quartz plate will now oscillate with the same period as the alternating cycle, and the amplitude of the oscillations will be a maximum when there is resonance between the frequency of the current and the natural mechanical frequency of the plate. Cady ⁽⁴⁸⁾ was the first to produce the resonance oscillations of quartz plates in this way.

Types Of Oscillations. Two types of oscillations ⁽¹⁹⁾ are possible on account of the longitudinal and transverse reciprocal effects (see figure 9):

- (a) Longitudinal elastic vibrations are emitted in the X direction which are called "thickness vibrations."
- (b) Longitudinal elastic vibrations are emitted in the Y direction which are called "length vibrations."

In the case of thickness oscillations, sound waves are produced which are emitted mainly in a direction at right angles to the surface

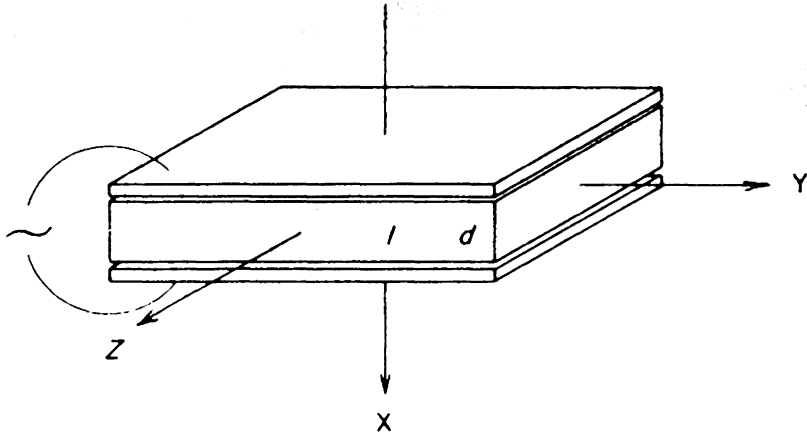


Figure 9

Crystal Plate and Electrodes

Bergmann, L. and H. S. Hatfield. "Ultrasonics." p. 15.
John Wiley and Sons, Inc., New York. 1946.

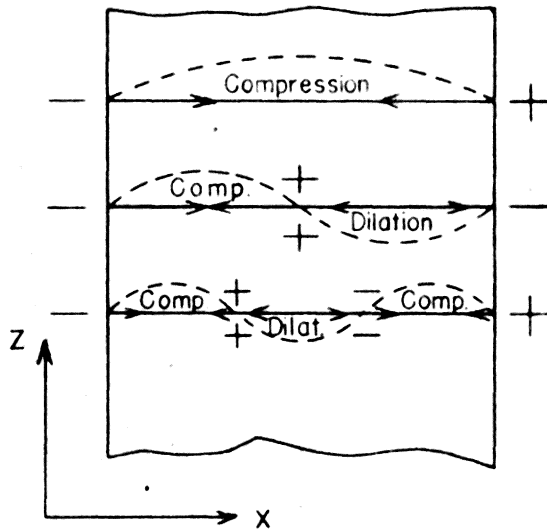


Figure 10

Overtones and Harmonics

Bergmann, L. and H. S. Hatfield. "Ultrasonics." p. 19.
John Wiley and Sons, Inc., New York. 1946.

of the quartz plate (19,174). Thickness vibrations are used in general for producing ultrasound from about 200 kilocycles to 50,000 kilocycles. In the former case a quartz plate of 13.6 mm thickness is used while in the latter case the plate is only 0.054 mm thick (19), for a frequency of 300 kilocycles a plate 1 centimeter in thickness is used (174).

Overtones. The quartz plate used for 50,000 kilocycles is very thin and often breaks when subjected to a powerful electric field. Consequently, in order to produce ultrasonic frequencies higher than 50,000 kilocycles no other course remains but to produce overtones in plates of a lower natural frequency. By doing this, the energy output of the plate then becomes less, but it may be excited with greater electrical energy without the risk of breaking the crystal (19,174). Bergmann (14) has shown that in quartz plates, whose surfaces are large compared with the thickness, the overtones follow the harmonic law when set into thickness vibration.

Excitation Of Overtones. Only the odd overtones can be excited very strongly, and even this depends on the way the quartz crystal is excited. Figure 10 (19), a section through a quartz plate in the XZ plane, shows the distribution of pressure and the oscillating motion in the plate for the fundamental vibration and in the second and third overtone. The dotted curve in the upper part shows the pressure distribution in the plate for the fundamental, assuming the electrodes on the right and left of the figure are charged with the signs indicated. The arrows show the direction of motion of the

parts of the plate. In the middle of the plate there exists a compression maximum, which changes to an expansion maximum after half an oscillation, the sign of the charges then being reversed.

The second overtone is represented by the middle curve. Here one has at the same instant, a position of compression and one of expansion. It may be seen from the signs of the charges as marked, that in order to bring about this condition equal charges of the same sign must be present on the external electrodes, and in the middle of the plate a charge of opposite sign. This is a state of affairs which cannot be practically attained in the case of a quartz plate.

This is no longer the case as regards the third overtone represented by the bottom curve of figure 10. Here a compression and an expansion region neutralize as regards their electric excitation, and oscillation is excited in the remaining compression region. Thus the odd overtones can always be set up, for all charges neutralize one another excepting those at the end of one-half wave.

Crystal Surface Movement. It is important for the radiation of sound from quartz plates vibrating in thickness, that the surfaces of the plates move to and from one another in a truly parallel manner -- that is to say, that they should behave like pistons, and not suffer changes of shape which would produce an uneven distribution of the radiated sound.

Unfortunately this does not occur. Dye (67), Skellet (133,134), Osterberg (140,141), and Straubel (193) have shown that when a quartz

plate is in thickness vibration, some parts of the plate surfaces take no part in the motion, while the amplitude of others is very variable. This uneven motion of the plate according to Bergmann (19), which is found also in the case of pieces of quartz perfectly homogeneous optically, is caused in the first place by the production of longitudinal oscillations in the plate on account of its transverse contractions. The irregularity of vibration frequently leads to destruction of the plate, for the elastic limit of the plate may be easily over-stepped in places of strong vibration, even when the load on the whole plate is relatively small. In addition, the modulus of elasticity E of the quartz in the YZ plane is not a constant, so that the natural frequencies of the longitudinal vibrations of a plate in different directions are very different. In this way, slight detuning may suddenly set quite different parts of the plate vibrating powerfully.

Epstein, Andersen, and Harden (71) state that an X-cut quartz plate does not give pure piston-like action because of small irregularities or imperfections in the quartz such as imperfect grinding, local twinning, impurities, etc.

Heating Effects. When ultrasound is generated considerable energy is evolved which always causes a large rise in temperature. Bergmann (20) states this rise in temperature is due to the large amplitudes of the quartz plate and unavoidable electric losses. He

states that this change in temperature will cause a certain change in frequency, but it will be a matter of minor importance in most investigations.

Properties Of Quartz, Technique of Cutting, Oscillator Mountings And Holders. Bergmann (20) and Cady (41) give a comprehensive review of the properties of quartz, technique of cutting plates, and oscillator mountings and holders. These topics, being beyond the scope of this investigation, will not be further elucidated except where necessary to describe other details of this work.

I. Propagation Of Ultrasound

Basic Physical Principles. Since the discussion of the understanding of ultrasonic phenomenon is still in development, the propagation of sound from the quartz crystal, through the transmitting medium, to the substance to be irradiated will now be discussed (174).

Light and sound are both wave motions which apparently obey totally different propagation laws. Light is propagated in straight lines whereas sound spreads out in all directions. It is known that this difference, however, does not lie in the laws of propagation themselves, which are moreover the same for both, but only in the different wave-lengths. When the wave-length is very small in relationship to a bundle of rays, all rays which do not belong to the straight line bundle, are eliminated by interference. In the

case of light with its very short wave-length, this condition is largely fulfilled, resulting in its straight line propagation. In sound, by contrast, even the highest audible sounds in air still have a wave-length of approximately 2 centimeters and in liquids up to 10 centimeters.

Schmid (174) described how to produce sound waves above the audible limit with correspondingly shorter wave-length and higher frequency. Because of its short-wave-length, this ultrasound can be produced in a straight line propagation which is similar in this respect to light waves.

Propagation. In the propagation of ultrasound, it first leaves perpendicularly from the circular quartz crystal into the oil in the form of a cylindrical ray. This straight line propagation is only true when the wave length (λ) is small in comparison to the radius, R , of the quartz crystal. The extent to which the ray deviates from the ideal cylindrical form can be easily estimated by the approximation formula, $\sin \theta = 0.61 \lambda/R$, which is valid for the condition that the wave-length is less than the radius. θ is the angle which the main ray makes with the imaginary straight cylinder. At a frequency of 300 kilocycles for example, the wave-length in oil and in water is approximately one-half centimeter. With a radius of 3.5 centimeters, the angle θ becomes approximately 5 degrees.

Reflection. If the sound strikes another surface, say the wall of the reaction vessel, a part of it is reflected. The amount of reflection depends of course on the angle of striking and can

therefore be totally reflected in a manner similar to light. In this discussion only a cylindrical sound ray striking a surface perpendicularly will be considered. It is naturally important to know how much sound can penetrate at all into the new phase and how much is reflected from the bottom surface of the container above the quartz crystal.

This can be easily estimated from the simple formula which assumes two media of infinite length: $R = (P_1V_1 - P_2V_2 / P_1V_1 + P_2V_2)^2$.

R is the fraction of the sound which is reflected; $1 - R$ is the fraction which goes into the new medium (bottom plate of reaction vessel); P_1 and P_2 are the densities of the two media (oil and reaction vessel material respectively); V_1 and V_2 are the velocities of sound in the two media (oil and reaction vessel material respectively). The product pV is designated as "sound hardness" and one can see that the reflection is determined only by the differences in "sound hardness" of the two media.

The difference in sound hardness of a liquid or solid as compared to that of a gas is obviously very great and one can easily see that at the interface between a hard medium and a gas, practically all of the sound will be reflected. The result of this is that air cannot be considered as a transmitter for ultrasound and the interface oil-air or air-vessel wall are practically non-transmitters of the sound. Therefore, the transmission must be

done without voids through the dense media and is best done by immersing the reaction vessel into the oil. Where this is not possible the sound can be conducted through other dense media.

At the oil-air interface with a strong reflection of sound waves, a noticeable effect is encountered which one does not recognize with ordinary sound. The sound exerts a pressure on surfaces from which it is reflected. Means of measuring this pressure will be discussed later. This sound pressure with high sound intensity which one encounters in ultrasound is so large that an ordinary liquid surface is completely deformed. By exciting a quartz crystal in an oil bath one obtains a light wrinkling or waving of the surface even at fairly low exciting power. Stronger excitation gives an oil fountain on the surface of the oil over the quartz crystal which can rise to 10 centimeters and single oil drops can be thrown much higher.

Even at the interface of liquid-solid, a large fraction of the sound is reflected. For example, for the surface oil to iron or steel one calculates a reflection of 88 per cent; for oil to glass, 70 per cent; for water to iron, 86 per cent; for water to glass, 66 per cent. The strong reflection is a desirable feature for underwater sound technique since a strong echo is desired, but it is very undesirable for transmitting sound into the reaction vessel.

Reduction of Reflection Waves. When dealing with transmissions through a plate, for example the bottom of a reaction vessel, the reflection is small in comparison to the wave-length of the

sound in the plate material. A thin walled glass reaction vessel does not offer too much resistance to sound of 300 kilocycles, but the wall must be very thin. Even at a thickness of $1/20$ of the wave-length of the sound in the wall material, the reflection has almost attained its maximum. The formula given above does not hold when the wall thickness is a whole numbered multiple (1, 2, 3, etc.) of one-half the wave-length ($\lambda/2$) of the sound in the wall material. In this case the wall plate vibrates in resonance and the reflection drops to a much smaller value -- theoretically even to zero. One should, therefore, construct the vessel bottom according to the general vibration formula, $\lambda = v/\nu$, where v is the sound velocity in the vessel material and ν is the sound frequency in the vessel wall. At a frequency of 300 kilocycles, one-half a wave-length in iron or steel ($v = 1,500$ meters/second) ≈ 0.85 centimeters; in glass ($v \approx 5,200$ meters/second) ≈ 0.87 centimeters; in ceramic or brass ($v \approx 3,600$ meters/second) ≈ 0.6 centimeters. Especially good transmitting conditions may be obtained when the thickness of all layers through which the sound must pass, that is oil bath, reaction vessel bottom, and reaction liquid, are equal to whole numbered multiples of one-half the wave length ($\lambda/2$). In this case the resonance of the entire system is especially good and very strong standing waves are formed.

J. Absorption Of Sound Waves

Absorption Hinderance To Sound Propagation. Besides the reflection at the interfaces previously discussed, absorption in the various media constitutes the main hinderance to sound propagation (174). The absorption of sound increases with the frequency and is, therefore, considerably greater for ultrasound than for ordinary sound. For an approximate estimate of the absorption, the formula $\alpha = \frac{16 \pi^2 \nu \eta}{3 v^2 \rho}$, may be used. v is the speed of propagation, ν the frequency of the sound, η the viscosity coefficient, and ρ the density of the medium.

The absorption coefficient, α , is defined through the equation $I = I_0 e^{-\alpha(x/\lambda)}$ where I_0 is the initial intensity, I is the intensity after passing through length x , and λ is the wavelength.

In order to have a better understanding of the formula, the distance s at which the intensity has dropped to one-half may be calculated. This becomes $s = \frac{\lambda}{2} \ln 2 = 0.013 \frac{v^3 \rho}{\nu^2 \eta}$. From this formula one can see that the distance s is greatly diminished with increasing frequency. This effect of decreasing s becomes especially great in the case of a gas in the ultrasonic range since the high frequency, low-velocity of propagation, and low density all work in the same direction. Very viscous liquids also absorb sound strongly. For example, it is found that an air layer of 0.4 meters thickness is sufficient to decrease the sound intensity of 300

kilocycles ultrasound at 20°C by one-half; for water, 440 meters are required; for transformer oil, 100 meters are required; for viscous paraffin oil, 3 meters are required. From these data one can again see that air is a very unsuitable media for transmission of ultrasound since it absorbs sound very strongly.

Conductors Of Sound. Solids and liquids are good conductors of sound as long as the coefficient of friction does not have a high value. By contrast, tough materials such as soft rubber, bakelite, and tar-like substances have been found useful as insulators against ultrasound. Very strong absorption is also obtained in powdered substances regardless of whether they are in air or in a liquid. In a similar manner as a transparent body becomes opaque to light by powdering, in the case of sound the multiple reflections from the surfaces of the powder grains leads to complete absorption in a short distance.

K. The Power Output Of A Quartz Crystal And Crystal Breakdown

Power Output. The maximum power output of a piezoelectric quartz crystal employed in an ultrasonic generator has been a subject of controversy among investigators in this field. Richards (156) has stated that "the shattering point of crystal quartz is reached with an output of the order of 3 watts per cm^2 if the crystal is 5 cm in diameter; the shattering point may be reached with an electrical input of 200 watts. A safe output is perhaps a fifth of this." Cady (46) recently stated that "the maximum power that can be radiated without

breaking the crystal depends on mounting, frequency, and medium. Wood and Loomis (208) recorded a value as high as 35 watts/cm². This is an extreme case; usually 10 watts/cm² is considered the upper limit, and even here there is danger of fracture." "Ten watts per square centimeter is 10⁹ times greater than the output from an average loud-speaker (80 db). At this power, with a frequency of 5(10⁸) cycles/sec, the amplitude of the pressure in the medium is 5 atm, maximum acceleration 10⁵ times gravity, maximal velocity 40 cm/sec, and radiation pressure 1,500 dynes/cm² = 0.0013 atm" (47). Oyama (142) "using a technique essentially similar to that of Wood and Loomis, reported a value of about 37 watts/cm²." This was the highest figure which three investigators (70) have found published in the literature.

Effect Of Crystal Holder Design. Epstein, Andersen, and Harden (70) have found "that by properly matching the impedance of the crystal electrically so that the voltage gradient is minimized, and by careful attention to holder design so that uneven stresses and other vitiating effects are avoided, appreciably greater power levels can be achieved." In a system designed to take these factors into consideration, these investigators have recently been able to measure power levels as high as 43 watts per square centimeter.

Causes Of Crystal Fracture. "The literature of ultrasonics contains many statements attributing crystal breakdown to the intensity of vibration, i.e., mechanical failure (72). It would appear that such an explanation is essentially correct, since the upper limit on

power density imposed by such factors can readily be computed from the elastic constants of quartz and the properties of the surrounding medium (200), assuming that Hooke's law is valid up to the breaking point. For X-cut quartz operating into insulating oil, levels of the order of 10^4 watts/cm² can be expected before mechanical breakdown of the quartz will occur.

"The reason for the failure of quartz crystal oscillators must be sought for in the electrical rather than the elastic properties of the system. Generally speaking, the upper limit on the power which can be radiated will be fixed by the dielectric strength of the surrounding medium rather than by the quartz. It is customary in the production of intense ultrasonics to immerse the crystal in an insulating fluid like transformer oil. When breakdown occurs in the oil, the intense localized heat in the resulting arc which follows the shortest path between the electrodes, along the surface of the crystal, produces uneven strains and consequently failure in the quartz. In experiments with more than fifty crystals operated under conditions which resulted in failure and destruction of the quartz, no evidence was observed of arcs through the body of the crystal. In every case when failure occurred there were greater or smaller chips at the surface and edges, with black carbonaceous deposits. The fact would appear to substantiate the hypothesis that dielectric breakdown of the oil at the quartz-oil interface is primarily responsible for the destruction of crystals.

"Further evidence supporting this line of reasoning can be obtained from a consideration of the relative dielectric strengths of quartz and insulating oil. According to the measurements of von Hippel and Maurer (200) at 25°C, the dielectric strength of quartz perpendicular to the axis is 5700 kilovolts/cm for a sample 0.05 mm thick. In comparison, insulating oils have a dielectric strength (110) of only one or two hundred kilovolts/cm."

Energy Transfer From Crystal. "To obtain maximum energy transfer from the crystal to the surrounding liquid in a direction such that this energy can be conveniently utilized, many workers (29) in ultrasonics have used an air box behind the crystal. It is possible from elementary considerations to show that by this device, there is practically total reflection of the wave emitted from the back side of the crystal, so that the amount of useful energy propagated into the surrounding liquid is doubled."

L. Measurement Of Acoustic Power Output

The presence of ultrasonic waves in liquids cause several phenomena which all observers report. The surface of the liquid on which the waves impinge becomes disturbed, and at high intensities is actually broken up into drops which may be thrown several feet. (If one wishes to demonstrate visually the action of sound waves (16,35,106), it has been observed that waves of relatively small amplitude are visible in liquids (144).) It is not yet

entirely clear how much this is due to actual radiation and how much it may be due to secondary electrical and mechanical pumping actions entailed by the generation of sound. Also, there is slow heating of the liquid apparently due to viscous absorption of sound.

Difficulties Encountered In Measurement. Chief among the difficulties in the undeveloped field of ultrasonics has been the lack of an entirely reliable measure of the intensity of the compressional waves. Several methods have been proposed which will be discussed here with their experimental objections.

In measuring the heating due to absorption, it is essential to eliminate dielectric power loss which, in early investigations, contributed to nine-tenths of the heating effect (163). The intensity of the waves may be measured either by modifications of the Rayleigh disk (7,8,26,33,194) or by total absorption in a solid such as pitch (160).

Richards (157) believes that the most obvious method of measuring intensity depends on maintaining a weighed reflecting surface in position by sound waves. A knowledge of the extent of surface, and of weight just insufficient for its displacement gives a direct estimate of the radiation pressure, and hence by straightforward means, leads to an evaluation of the energy density, internal temperature differences, etc. in the liquid.

Methods Of Measurement. Wood and Loomis (206) describe an experiment in which an 8-centimeter glass disk supported 150 grams in irradiated oil. Several very different modifications of this

principle were employed without obtaining reproducibility of more than order of magnitude in any case. Success in this method depends upon a regular standing wave system, and failure may be attributed to its absence. Not only are the large amplitude vibrations of the quartz crystal far from pure, but reflections from the walls and other secondary phenomena produce a complex and shifting interference pattern in the liquid.

Several phenomena described by Richards and Leemis (162) are amenable to quantitative treatment, but none of them are fitted to the measurement of sound intensity. The ebullition of liquids immediately below their boiling points and the cavitation of air in liquids are unsuitable, because both require too great precautions for routine measurement, and because they give no direct information concerning forces in the liquid. The emulsification of one liquid in another has, under suitable conditions, been shown (163) to be reproducible, but yields results of little value since it is due to transverse waves in glass vessels and not to compressional waves in liquid itself.

An attempt was made to measure sound intensity by the rise in temperature of a totally absorbing body. One-half of a set of copper constantan junctions were wound with rubber, and the other half encased in a thick glass tube. Both were then placed in the irradiated liquid and the difference in potential between them measured. The absorbing elements maintained a considerably higher temperature

than the reflecting element, but owing to irregular convection currents in the liquid and to lag in heat transmission through the rubber casing, the difference in temperature was not clearly indicative of small differences in sound intensity.

The heating of liquids, notably water, has already been employed (162) as a rough measure of relative sound intensity. This phenomenon is, however, extremely complex, and is not suitable at present for exact work in this connection. High frequency fields produce a dielectric loss in the liquid which manifests itself as heat, and hence scrupulous electrical shielding is essential. Moreover, it is not at present clear how much sound is converted into heat per unit path through the liquid. If the measurement is made in glass vessels, reflection phenomena and the transverse waves in glass make the conditions so complex as to be wholly incalculable. Finally, the absorption of sound by a liquid, due to the deviation from perfectly adiabatic conditions in its transmission, involves changes of temperature so small as to require a very refined technique for their detection.

It appears that Epstein, Andersen, and Harden (69) take exception to the work by Richard and Loomis (157). Richard and Loomis stated above that if the measurements were made in glass vessels, reflection phenomena and the transverse waves in glass make the conditions so complex as to be wholly incalculable. Epstein, Andersen, and Harden employed a colorimetric substitution method. In their work, an X-cut plane circular quartz crystal was mounted

in an air backed holder and placed at the bottom of a heavy walled cylindrical glass "jar, concentric with the axis. This was driven by a specially designed crystal stabilized radio frequency generator and a tuned inductance capacitance network was used to match impedances. The glass jar contained about 10 liters of transformer oil as the insulating fluid. Mounted in the bath eccentrically, so as not to interfere with the crystal, were (1) a mechanical stirrer, equipped with a series of propeller blades and operating at about 300 rpm, (2) a 500-watt immersion heater, and (3) a 10-junction copper-constantan thermocouple by means of which the difference in temperature between the oil bath and the surroundings (room temperature) could be determined.... The stirrer operated throughout all the measurements, and was necessary to obtain temperature equilibrium through the oil bath. The immersion heater was used only for calibration,.... but was left permanently mounted so that the heat capacity of the system remained unchanged during the series of measurements.... With the stirrer running and the crystal operating, the temperature rise, as recorded by the thermocouple, was measured, taking readings every 15 seconds. The thermocouple readings were linear with time for periods of observation up to 10 minutes. The slope of the curve thus obtained $d \Delta T / dt$ (where $\Delta T = T_{\text{bath}} - T_{\text{room}}$) was computed by the method of least squares and was taken as a measure of the power output of the crystal. In order to convert this to an absolute basis the bath was allowed to cool to room temperature, and with rf turned off, energy was supplied to the

immersion heater. A stabilized 60-cycle, 115-volt line controlled by a Variac was used, and a calibrated wattmeter, measured the power input to the heater. A series of ΔT versus t curves were taken with this arrangement at fixed values of wattage, and the slopes of the straight lines thus obtained again computed by least squares.

A plot of $d \Delta T/dt$ against watts input to the heater was linear and passed through the origin. From it the power output of the crystal could be interpolated By linear interpolation of these data, the crystal output comes out to be 327 ± 4 watts or 65 per cent 'efficient' with the discrepancy due almost entirely to losses in the impedance matching network."

The method of measurement used by Epstein, Andersen, and Harden "depends essentially on the fact that the sound produced is confined to the system since the acoustic impedance of air relative to oil and glass would practically prohibit transmission out of the jar. The figure given 'for the efficiency of the unit' is a measure of total power rather than acoustic power, but is comparable with previous high intensity measurements which also did not separate heating effects due to the sound from those produced by other means."

Richards (159) describes three further principles for measuring sound intensity in liquids. Although the first two methods are unsatisfactory they are indicative of sound wave effects. "The first depends upon the change in volume of small manometric bulbs. Thin bulbs with flattened sides were blown on smallbore, soft glass

capillary tubes, calibrated against known pressure differences, and subjected to sound radiation. Volume changes corresponding to pressure of 0.5 mm mercury were noted, but these were considered unsatisfactory because, in order to indicate absolutely the radiation pressure, the surface of the bulb must be totally reflecting. Moreover, when sufficiently sensitive to register more than the order of intensity of radiation, the bulbs were so fragile they exploded under the influence of sound waves.

"The second principle is quite different, and depends upon the retardation of flow of a liquid in a capillary tube. The rate of flow being a function of the difference of pressure which causes it, it is possible to construct a modified viscosimeter which gives results of almost any desired sensitivity" The gauge was "abandoned for two reasons: firstly, it was found possible, with sufficiently high sound intensities, to cause an upward or reverse flow in the capillary tube, and secondly, resonance phenomena in the column of liquid were found to play so important a part that, even with low sound intensities, the flow was sometimes indefinitely arrested."

The third principle discussed by Richards (159) is the ear-trumpet principle. This method depends upon "concentrated sound energy being measured as hydrostatic pressure. A small funnel was blown on the end of a fine capillary tube and immersed in the liquid radiated. The upward displacement of the capillary meniscus gave a measure of the sound-wave intensity. This device was tested with

sound waves of frequencies between 250 and 500 kc, and intensities varying from that produced by a crystal driven by a 7-watt tube to 1 kw driving energy Its behavior was perfectly consistent over this range This measurement demonstrates two points of interest: first, that the gauge might be used, if it seemed profitable to develop it to the necessary degree of precision, to measure the coefficient of absorption in a liquid; and second, that tuning effects may play a large part in the magnitude of the upward displacement of the meniscus.

Tuning Effects. "Tuning effects are of two types. The first, of specific resonance phenomena in the capillary column, and causes a jerky upward motion which takes some seconds to attain its full magnitude. This appears to cause no serious error in the ultimate readings; possibly the strong heating of liquid in the neighborhood of the capillary meniscus facilitates, by lowering the surface tension, the adjustment of the gauge.

"The second type of tuning is caused by variations in the position of the funnel in the standing wave in the main body of radiated liquid Enormous differences in deflection at uniform intensity may be traced to this effect, and it is obviously important to adjust the funnel, when regular standing waves are present, to a position of maximum deflection in order to secure comparable results for different intensities. When, as in glass test tubes, the wave pattern is extremely complex because most of the energy is transmitted to the liquid by transverse waves in the glass, tuning effects are more

erratic, and only by replacing the funnel exactly in the same position in the same tube in a constant volume of water may reasonably comparable results be obtained Variations in the properties of funnels of different configurations are considerable; a thick-walled funnel of roughly exponential form appears to be most satisfactory."

In all of the methods described above for measuring sound intensity, only a relative and not an absolute measure is intended.

M. Effects Caused By Ultrasonics

Cavitation. By far the most important consequence of the passage of intense sound waves through liquids is cavitation (34,36,109). Cady (49) states its presence in liquids traversed by ultrasonic waves was first investigated by Boyle and his associates. He defines cavitation as a term applied both to the liberation of bubbles of air or other absorbed gases from a liquid and to the tearing apart of the liquid itself with the production of hollow spaces filled with vapor. These hollow spaces, in the form of layers a wave-length apart, collapse with great violence due to the external pressure. Bubbles of absorbed gases liberated also collapse to some extent.

Optimum Pressure For Cavitation. Cady (49) states that the optimum pressure for pronounced cavitation effects is about two atmospheres pressure, but at atmospheric pressure this effect sets in at intensities of about 0.03 watts per square centimeter in the ultrasonic range (49,37). Its importance lies in the fact that

almost all of the phenomena to be described subsequently, disappear if easily visible cavitation is suppressed, either by degassing the liquid, or by applying to it a large hydrostatic pressure (97,111,126,179,195).

Degassing By Cavitation. Cavitation has been shown to exist in a degassed liquid very near its boiling temperature (162), but only one observer has reported it in pure water at room temperature (188), and he finds not easily visible bubbles, but opalescence. Since the gas bubbles formed by cavitation do not redissolve, but rise jerkily to the surface, the most obvious result is degassing of the liquid. This is a gradual process however, unless the liquid is radiated many hours. If this is done the volume of gas liberated per unit time appears independent of time (162,192).

Paunov (147) has found that under the influence of ultrasonic frequencies the amounts of absorbed gas decrease to approximately fifty per cent of the original amount. This is explained by the assumption of standing waves in the water undergoing no change in gas concentrations in the nodes, but with the antinodes completely outgassed.

The degassing of metal melts has been reported to have valuable technical applications (15).

Physical And Physico-Chemical Effects Caused by Ultrasonic Irradiation. One of the most spectacular concomitants of cavitation is the faint luminescence of liquids which was first discovered in water (85,214). Chambers has found the intensity of light to be

proportional to the product of the dipole moment of the liquid and its viscosity (52). Several observers report that the luminescence originates at the liquid-gas interface of the cavitated bubble (52,77,122). This is a very fundamental observation, since it shows that enough energy is produced locally to give visible light of 6×10^{14} cycles per second frequency. Sound waves of frequency less than 10^6 per second cannot cause this by any primary process.

Bresler (39) used a luminol-sodium carbonate solution to study cavitation. He found that an increase of pressure to 2.5 - 3.0 atmospheres quenched luminescence in the ultrasonic field while hydrodynamic cavitation with a much longer oscillation period than ultrasonic cavitation produced no luminescence. By the addition of substances with a high vapor pressure, such as ether or ammonia, the breakdown of the cavitation bubbles is prevented, and the luminescence of luminol otherwise produced by ultrasonic vibrations is prevented. It was concluded that ultrasonic luminescence in the presence of air is due to direct activation of oxygen and not to hydrogen peroxide first formed.

The acceleration of chemical reactions by intense sound has also been shown to be due to cavitation (77), and there is some evidence that depolymerization results in certain liquids (194). The great majority of reactions involved are oxidations such as the

conversion of iodine ions into iodine molecules (23,125), but effects on hydrolysis (162) and on inversion of cane sugar (187) have also been reported.

An important member of the group of phenomena produced by cavitation is the formation of colloidal systems, more especially the emulsification of one liquid in another (62,129,187,207). This in distinction to the acceleration of oxidation reactions, is usually independent of the identity of the cavitating gas. The emulsification of various liquids, including mercury (207), in water has been reported by many observers, and studied in detail. Heavy liquid metals such as mercury and gallium do not appear to require cavitation in order to be emulsified (30,31,32,97,153,154,170). The emulsions produced are often more stable than those produced by colloid mills or similar devices. There appears to be a small group of technical products, ranging from cosmetics to photographic plates, which can be produced in better quality by ultrasonic emulsification than in any other way (57,61). Colloidal metals have been produced by subjecting the cathode to sonic vibration during electrolysis, and by analogous procedures (59,177). Many inorganic and organic sols (172) and gels (87) are peptized by ultrasonic waves without the presence of peptizing agents. On the other hand, coagulation will result if the particle size bears a certain relationship to the acoustical wave-length (40,143,189). Flow orientation of unsymmetrical particles occurs at small intensities.

This may readily be demonstrated with aged vanadium pentoxide sols between crossed Nicol prisms (40). Also natural thixotropic gels are liquefied by the motion and local heating of the medium.

Several other physical and physico-chemical effects which have been demonstrated (162) should be mentioned. Explosives are detonated not only in liquids, as mentioned above, but also on vibrating glass surfaces in air. Sound waves will alter sensitive metastable systems, such as for example, the yellow to red enantiotropic change in mercuric iodide at room temperature. Superheated liquids break into almost explosive ebullition on radiation with intense sound (162).

Undercooled liquids and superheated solutions are forced to crystallize by intense sound, but only under restrictive conditions (155). There have been conflicting reports about this (192,207) crystallization, but it has long been known that many liquids, such as benzophenone, remain undercooled indefinitely at room temperature, but recrystallize readily if melted and preheated only a few degrees. When the preheating has been higher, no amount of shaking produces crystallization; when the preheating has been low, shaking produces the immediate appearance of crystals. The presence of certain adsorbing substances, such as carbon or clean glass, requires that the preheating shall be far higher than if they are absent. Often dust, which has been included by accident and is of unknown composition, serves as the adsorbent; many liquids will not crystallize at any temperature if they have been passed

through sufficiently fine filters and sealed in flamed glass tubes. The role of ultrasonic waves is exactly equivalent to shaking. When the liquid may be caused to crystallize in a sealed glass tube by shaking, ultrasonic waves will also cause it to crystallize, but if it has been sufficiently preheated, neither will have any effect. Another aspect of the influence of ultrasonic waves on crystallization is the decrease in grain size of metals on acoustical treatment of the crystallizing melt (176,181). This is to be expected with all crystallizing substances, since the sonic agitation shears off small particles of the growing crystals, and these particles act in turn as nuclei.

The sonic irradiation of metals which are in the passive state is sometimes to increase the passivity and sometimes to relieve it. Similarly, metals which are cathodically polarized during electrolysis are depolarized by sound if the current density is low (175). Some polarized electrodes are microphonic (139). The quality of some electrolytic deposits is improved by sonic irradiation during electrolysis (213). The fogging of photographic plates in a standing-wave field has been reported by Marinnesco (132,131), who attributes it to sonic activation of molecules; the ballo-electrical hypothesis previously discussed accounts for this. It has also been shown that the electrical conductivity is increased and the electrical breakdown voltage diminished in a standing-wave field (136).

Numerous biological observations have been made since the beginning of ultrasonic history (9,211). Blood is laked (53,97).

small animals are killed (27,111) and organisms such as paramecia, algae, and many other bacteria are destroyed (54,99,100,101,178,203). In laboratory tests (128), sound waves have reduced the bacteria count of milk to 8 per cubic centimeter, while a count of 30,000 indicates a high standard of purity for pasteurized milk. Should complete sterilization of foods by sound waves become commercially practical, a revolution in food distribution would be in order. Containers of milk could be shipped anywhere and kept for months, and fruits and vegetables could be canned or packed fresh without heat. All of these effects appear to depend largely on cavitation.

The reduction of curd tension in milk has been studied (50), and many dairies use sonic treatment in the preparation of infant's milk. In this process (128) the fat globules are broken into smaller sizes, which remain in suspension instead of rising to the top of the liquid. The result is a milk which forms into smaller curds in the stomach. The influence of cavitation on the activity, stability, and degree of dispersion of several proteins (55,76) including some pepsins (51), has been studied. Chambers appeared to have made an especially valuable discovery when he demonstrated the sonic extraction of some labile bacterial constituents (56). However, he later found that the method was not of as general value as was to be hoped (164,173).

Several therapeutic suggestions for the use of ultrasonic waves have been made (84,88) but none seems to have yielded results of general value. Exceptions may be found in pioneer work done in

Germany by Fohlsan, Richter, and Farow (123). In fourteen cases suffering from severe sciatica and plexus neuralgia, treatment of the affected parts by ultrasonics benefited all but two. A number of apparent cures have been reported where all other methods of treatment have failed.

The use of ultrasonic waves to perform knifeless surgery has been explored by Lynn and Putnam (124) at Columbia University. Similar work is under way at the Institute of Living at Hartford, Connecticut. Lynn and Putnam performed brain operations of various sorts, without opening the skull, on thirty-seven cats, dogs, and monkeys. Sound waves far up in the ultrasonic range (800 kc) were used. In this work, a curved crystal which focused the sound waves to a sharp point were employed. The scientists found that they could stimulate temporarily, or destroy a selected bit of brain tissue.

The work is still in its early experimental stages, but it suggests interesting possibilities of knifeless surgery on the human brain. Prefrontal lobotomy, a drastic operation in which the frontal lobes are cut off from the rest of the brain, has been used as a last resort to relieve some 2000 incurable mental patients in the United States. With further refinement of a new technique, such an operation might eventually be performed in a few seconds by sound or shock waves.

Other scientists have been attempting to use sound as a weapon capable of killing or disabling man. Simon (125) of the

Aberdeen Proving Grounds found such a weapon in a small experiment station near Lofer, Germany. Here sonic guns of various types had been built during World War II by Wallauschek. In the latest and best design, sound in the audible range was generated by the rhythmic explosion of gas in a siren-like metal tube, and the waves focused on the target by a parabolic reflector. No battle tests had been conducted, but it was estimated that at 50 meters the bunched waves would kill a man in 30 to 40 seconds. At 300 meters it was estimated that the effect would be very painful and would probably disable a man for some time. Vision would be affected, and points of light would appear as lines.

Manchester (123) discusses other uses of ultrasonics. He states that ultrasound is used to detect hidden cracks and flaws in metal castings up to ten feet in thickness. It has been found that flawless castings subjected to ultrasound gives characteristic echoes which can be picked up by sensitive instruments and amplified. A "sour" note will show the presence of an imperfection and may be located by electronic devices. X-ray machines may be used for the same work, but hours are usually spent where ultrasonics can do this in a matter of seconds. The new ultrasonic detectors are versatile in that they may be mounted on assembly lines to sample-test metal, plastic, and ceramic products.

As an extreme usage, ultrasonic laundering of clothes has been suggested by Appleton (128), the secretary of Great Britain's Department of Scientific and Industrial Research. He says that high frequency vibrations would shake dirt from fabrics and help to emulsify it in the suds.

In a Texas plant (151) where carbon black is manufactured, a sound generator is installed in a flue. The sound vibrations create collisions between carbon particles which cause them to roll up like snowballs and fall, instead of being carried out and wasted. The machine is also being installed in chemical plants which exit toxic fumes to prevent their escape.

Ultrasonics (151) is being tested to hasten the drying of powdered milk, soap, and drugs. The liquid is sprayed through the top of a tower and dehydrated by hot air as it falls. Sound agitates the falling particles and causes quicker evaporation.

Oxidation Reactions. Richards and Loomis (162) have observed the oxidation of potassium iodide when subjected to high frequency sound waves. This oxidation reaction was confirmed by Beuthe (22). He found that after ten minutes action of ultrasonics on pure distilled water, hydrogen peroxide could be detected by titanil sulfate. A 1/1000 normal solution of potassium permanganate which has a faint pink color showed after ten minutes action of ultrasonics, a color change to brown. This was caused by the formation of manganese dioxide.

Beuthe found that hydrogen peroxide is only formed in water saturated with air or oxygen. This observation explained the fact that all the oxidation reactions observed took place only in water containing air, if at the same time the formation of bubbles occurs. The question that arose is that of the source of energy necessary to dissociate the O_2 molecules dissolved in the water in order to cause a formation of H_2O_2 . Beuthe postulated the following process to take place. "The vibratory motion of gas bubbles produced by the ultrasonic waves causes O_2 molecules to be ionized at the comparatively large boundary between liquid and gas, perhaps by the action of electric charges. The O atoms thus formed are then absorbed by the water with formation of H_2O_2 ." Further work by Beuthe showed that nitrogen dissolved in water gives in the same way nitrous acid and ammonia when subjected to ultrasonic waves.

Schmitt, Johnson, and Olson (178) arrived at results similar to those of Beuthe. They showed that "if an aqueous solution containing dissolved oxygen is radiated, hydrogen peroxide or something is formed". To ascertain whether the oxidation occurred during the process of cavitation, on the assumption that the formation of an interface is essential to the activation of oxygen molecules, the author's experiments were carried out with aqueous solutions of potassium iodide containing very small amounts of dissolved air. Iodine was liberated although no bubbles were seen. Moreover,

bubbling oxygen in a fine stream during radiation through an aqueous solution of potassium iodide and starch which originally was gas-free, did not give rise to a color, apparently since none of the oxygen dissolved.

The investigators saturated an aqueous solution of potassium iodide and starch with oxygen under four or five atmospheres of pressure and then on releasing the pressure, no oxidation of the iodide ion occurred. Therefore, it was concluded that the mere formation of bubbles in the absence of ultrasonic vibrations is unable to effect the oxidation.

"On the other hand, if solutions of potassium iodide or of hydrogen sulfide containing air were radiated for the same time at a series of increasing pressures applied from an oxygen tank, it was found that the amount of reaction as measured by the depth of color or opalescence, respectively, slowly increased up to a certain pressure and above this critical pressure there was a sudden diminution in the reaction rate. The depth of color produced by three minutes exposure increased somewhat with pressure, so that at a pressure of thirty-five pounds per square inch the color was definitely darker than at atmospheric pressure. Under these conditions no visible cavitation occurred during radiation. At fifty-five pounds the depth of color was still maintained, but on increasing the pressure pound by pound, a series of fainter and fainter colors was produced until at sixty-five pounds per square inch no color could be detected after three minutes radiation. The critical

pressure above which no measurable reaction takes place is an arbitrary figure depending chiefly upon the amount of dissolved gas and upon the intensity of radiation. The fact that the color intensity increases slightly with pressure up to a certain point is to be expected. Increased pressure, the prevention of loss of reactants by cavitation, and the subsequent minimizing of disturbances in the standing wave system produced by the larger bubbles all tend to augment the amount of reaction taking place during the period of radiation. The fact that higher pressures inhibit the reaction completely is a powerful argument against the hypothesis that individual oxygen molecules in solution can be activated directly by ultrasonic energy. A possible explanation of the phenomenon is that there exists a critical bubble size below the limits of visibility, which is essential for the activation of the oxygen. Application of pressure beyond a certain amount prevents the cavitation of bubbles of this size and consequently inhibits the reaction. A pressure of seventy pounds per square inch does not affect the rate of oxidation of potassium iodide by hydrogen peroxide. The effect of pressure, therefore, must be on the rate of formation of hydrogen peroxide, if this be the active agent.

The rise in temperature caused by exposing a test tube containing 10 ml of water at room temperature to three minutes of radiation was about 5°C, both under atmospheric pressure and under an applied

pressure of seventy pounds per square inch. In the latter case, cavitation of air was prevented, and the piling up of water at the meniscus noticeable increased. Yet, oxidation did not occur under these circumstances."

Parthasarthy and Pande ⁽¹⁴⁶⁾ state that the reaction velocity of a number of chemical processes is enhanced under the influence of ultrasonics. In the paper by Parthasarthy and Pande, it is stated that Bethue (Beuthe ⁽²²⁾) was able to separate iodine in the case of the oxidation of potassium iodide by a ten-minute "dose" of ultrasonic irradiation. Bibliography item 52 in the paper by Parthasarthy and Pande gives the name of H. Beuthe (Beuthe ⁽²²⁾) which is not consistent. Cross-checking with the work entitled "Ultrasonics" by Bergmann and Hatfield ^(22,24), the author of the publication to which Parthasarthy and Pande made reference is given as H. Beuthe. Apparently the reference to Beuthe is an error in copying the literature review by Parthasarthy and Pande, since Chemical Abstracts ⁽²⁵⁾ also gives the author of the publication as H. Beuthe.

Investigations by Liu and Wu ⁽¹²⁵⁾ confirmed the presence of hydrogen peroxide by exposing a dilute solution of potassium permanganate (about 0.002N) to radiation. The permanganate was decolorized. Addition of potassium permanganate to water which has been radiated showed the same result. Since hydrogen peroxide

is the only substance which can be formed from oxygen and water and is capable of decolorizing permanganate, they concluded their observations as proof of the production of hydrogen peroxide under the influence of radiation.

The amount of hydrogen peroxide formed in 8 ml of water after seven minutes radiation was found to be about 0.006 mg. Taking the amount of oxygen dissolved in water from air to be 6 ml per liter, 0.15 mg of hydrogen peroxide should be produced if all the oxygen dissolved in 8 ml of water is converted into hydrogen peroxide by radiation. Hence only about four per cent of the oxygen is converted into hydrogen peroxide under the conditions of the experiment.

The investigators also studied the effect of electrolytes upon the production of hydrogen peroxide. In acid (N/10 HCl, H₂SO₄, or H₃PO₄) solutions, the amount of hydrogen peroxide formed in eight minutes of radiation is about five times as much as in distilled water, salt or alkaline solutions of the same concentration.

Schmitt, Johnson, and Olson (176) found that when carbon tetrachloride was added to potassium iodide and starch solution, an intense blue color developed immediately upon radiation. Liu and Wu (125) have shown that chloroform is just as effective. To test whether the formation of hydrogen peroxide can account for such a reaction, a solution of 3 per cent hydrogen peroxide was added to the chloroform-potassium iodide-starch mixture without

exposing to radiation. No immediate development of color was observed, even when a large amount of hydrogen peroxide was added. This proved that peroxide formation cannot account for this reaction.

Addition of potassium iodide-starch to a mixture of chloroform or carbon tetrachloride and water after irradiation also gives the iodine reaction immediately. Addition of silver nitrate gives a positive test for chloride, while a mixture of 3 per cent hydrogen peroxide and carbon tetrachloride or chloroform without radiation gives a negative test. It is clear from these observations that chloroform or carbon tetrachloride does not act catalytically in the oxidation of potassium iodide, but is itself decomposed, giving rise to some free chlorine.

Potassium iodide reacts with ozone and hydrogen peroxide while potassium permanganate reacts with hydrogen peroxide but not with ozone. If there is any ozone present, iodine titration should indicate more oxidizing power than potassium permanganate titration. Liu and Wu (125) compared iodine titration with potassium permanganate titration. Several portions of the irradiated water were mixed and divided into two portions. One was titrated immediately with potassium permanganate and to the other potassium iodide was added. After standing for one hour, the iodine liberated was titrated with 0.002N thiosulfate. The amounts of the oxidizing power calculated from the two titration values were identical within the limit of experimental error (about 5 per cent). If there is any

ozone produced by radiation, the amount cannot be more than one part in 20 million. Such a small amount of ozone certainly cannot account for any of the oxidation observed.

The oscillating circuit used by Liu and Wu ⁽¹²⁵⁾ is described. ⁽¹²⁶⁾ The vibration of the quartz plate was adjusted to vibrate at the rate of 1.4×10^6 times per second for all work done by these investigators. Solutions to be radiated were placed in a small thin test tube 15 mm in diameter. The tube was clasped so that its bottom was buried in the mound of the vibrating dielectric. When this was done, vigorous vibration and cavitation were set up inside the tube. The intensity of radiation was found to vary with the thickness, the shape, and the position of the test tube in the dielectric even though the power input was kept constant. The results selected for comparison were, therefore, made by using the same test tube at a fixed position. Temperature was kept between 25-30°C by means of a cooling coil described ⁽¹²⁶⁾.

Liu and Wu ⁽¹²⁵⁾ showed that oxygen is necessary for ultrasonic oxidation, and that the amount of hydrogen peroxide, the only oxidising agent formed during radiation, cannot account for all the reaction observed. They concluded that "oxygen is directly activated under the influence of ultrasonic radiation. Cavitation being essential, it is clear that only the oxygen molecules on the surface of the bubbles are active during radiation. As soon as radiation ceases, the activity of the oxygen disappears. The

active oxygen can liberate iodine from iodide or react with water to form hydrogen peroxide. When carbon tetrachloride or chloroform is present, it reacts with the active oxygen to give free chlorine."

Schultes and Gehr (180) state that "ultrasonic waves of 540000 hertz" (540 kilocycles) "produce hydrogen peroxide in a concentration of about 0.5 mg per cent in water saturated with oxygen." When water is saturated with air and then subjected to ultrasonics, nitrous acid is formed in addition to hydrogen peroxide. The nitrous acid is oxidized to nitric acid under the action of ultrasonics if sufficient oxygen is present.

Kusano (116) reported that when ultrasonic waves were generated by a quartz plate cut at right angles to its electrical axis and subjected to varying potentials from a power source, iodine was liberated from potassium iodide in 1 per cent aqueous solution. The degree of liberation varied directly with duration of irradiation from 0.5 minutes to 10 minutes and also varied directly with increase in voltage of the primary circuit from 800 to 1200 volts and thereafter decreasing with increasing voltage. The ultrasonic waves produced at 1000 - 2000 volts slightly increased the concentration of hydrogen peroxide in dilute aqueous solutions owing to an oxidation of water to hydrogen peroxide. This sample was subjected to the ultrasonic waves for one minute.

Kling and Kling (113) state that double distilled water free of dissolved air does not acquire oxidizing properties by

irradiation with ultrasonic waves of frequency 985,000 cycles per second. Hydrogen peroxide and ozone are produced by irradiation of water containing dissolved oxygen. Irradiation of water containing dissolved air also produces nitrous and nitric acids.

Loiseleur (127) has found that ultrasonic irradiation activates oxygen dissolved in the water with the formation of hydrogen peroxide or the oxidation of acceptors in the solution. A treatment of a few minutes turns Nadi reagent blue and causes pyrogallol to turn yellow. The change of a 5 per cent dihydroxyphenylalanine solution at pH 6.5 to a rose color is very appreciable after a treatment of 1 minute. In this connection it is interesting to note that in certain experiments conducted by Schmitt, Johnson, and Olson (178) it was found that dye molecules were altered by ultrasonic radiations. When Brom Thymol Blue was subjected to ultrasonic radiations a color change was effected. It was suspected that the indicator itself was affected, rather than that the reaction had been stimulated. Subsequent tests showed that when a dilute aqueous solution of Brom Thymol Blue (to which sufficient sodium hydroxide was added to produce a blue-green color) was radiated, the solution changed to yellow in a very short time. It was easy to demonstrate that comparatively few of the dye molecules were destroyed in the process of radiation, for addition of an alkali caused a prompt return of the blue color. Other indicators, such

as Brom Phenol Blue and litmus were affected in a similar manner. Whatever the process may be, there is no doubt that dye molecules were altered by the radiation and gave rise to hydrogen ions.

These observations are strong argument against placing indicators with solutions to be tested or studied in the presence of ultrasonic irradiation, as wholly unreliable conclusions may be reached.

Soloveva (190) has found that ultrasound of 394,000 hertz (394 kilocycles) catalyzes the oxidation of aqueous potassium iodide to potassium iodate and of ferrous sulfate to ferric sulfate by atmospheric oxygen. The greater the sound intensity the more rapid the oxidation, but the proportion is not linear. Measurements of the amount of hydrogen peroxide formed in water under similar conditions indicate that the hydrogen peroxide formed (less than 0.002 per cent) cannot be the primary step in the process. The quantum efficiency of ultrasonics is very low, so the effect is probably due to local concentrations of energy.

Solovjeva (191) found oxidation of potassium iodide to potassium iodate when subjected to ultrasonic waves. He stated that ferrous sulfate in Mohr's salt was oxidized to ferric sulfate, but that no hydrogen peroxide is formed with water. This is the first article located in the literature research that states no hydrogen peroxide is formed with water when subjected to ultrasonic waves.

The reader's attention is invited to the discrepancy in the spelling of Soloveva (190) and Solovjeva (191) as reported in the American and British chemical abstracts respectively. The American abstracts report the formation of hydrogen peroxide being formed in water, while the British abstracts report no hydrogen peroxide is formed in water. Apparently, this disagreement is due to the translators since the original paper referred to in both cases is identical.

Urasovskii and Polotakii (199) studied the kinetics of 0.1 and 0.04N trichloroacetic acid ($\text{Cl}_3\text{CCO}_2\text{H}$) in aniline and non-polar gasoline in the presence and absence of ultrasonic waves at $50 \pm 0.2^\circ\text{C}$ for 30, 60, 90, 120, and 150 minutes. The ultrasonic waves were obtained from a piezo-quartz oscillator. The diameter of the quartz disk was 50 mm and the thickness was 4.00 mm which corresponds to a resonance frequency of 500 kilocycles. The quartz disk was suspended in transformer oil and the temperature of the oil maintained at $50.0 \pm 0.2^\circ\text{C}$. The kinetics of isomerization of NH_4ONS melting at 170°C were similarly investigated. In all of these cases no effect of ultrasonics was observed. So the investigators concluded that the chemical action of ultrasonic waves observed by other workers is a secondary effect of the substances produced in water in the presence of dissolved air (H_2O_2 , HNO_2 , or HNO_3) by the action of ultrasonic waves upon water.

Wood (205) states that Fiesdorff, Chambers, and Malisoff obtained chemical reactions resulting from ultrasonic irradiation reported by

previous observers. They investigated the previously disputed point as to whether the formation of hydrogen peroxide from the activation of oxygen dissolved in the water was responsible for some of the chemical changes which had been observed. They proved conclusively that such activation occurs only during sonic cavitation and only in the immediate vicinity of such disruptive disturbances. They stated "from the evidence at hand we may conclude that oxygen is brought into a reactive state during some phase of cavitation through a process not understood at present. The activated oxygen is then free to react with either solute or solvent molecules. One may assume perhaps that molecules of the high energy necessary to permit the formation of hydrogen peroxide from molecular oxygen and water are created during sonic cavitation through a process of ionization or excitation. While no theoretical justification for such an hypothesis can be drawn from acoustical theory it should be remembered that, in the events accompanying cavitation, we are not dealing with acoustical phenomena per se. As a matter of fact, the recent observations by Chambers that visible light is emitted from pure polar liquids during cavitation by sound waves of the same amplitude as those used in our experiments, lends credibility to the supposition that excitation or ionization may actually be occurring. Whatever the mechanism, it would appear from the evidence in hand that activation of oxygen during cavitation offers the best explanation for chemical changes recorded in our experiments."

Recent work by the Audouin's (3) has shown that commercial oleic acid subjected to ultrasonic radiations reduces the iodine number and increases the hydroxyl value. This indicates that the effect is one of oxidation.

Explanation Of Cavitation. Several explanations have been advanced for the acceleration of chemical reactions, but none of them can here be accepted with any enthusiasm. The first (162) attributed the acceleration to a direct temperature effect. This resulting adiabatic temperature change has been shown (162) to be less than 0.01°C , and therefore is too small to influence any known reaction appreciably.

Rayleigh (30) has shown that high pressures accompany the collapse of bubbles. It might be argued that pressure surges from this cause are sufficiently great to cause the adiabatic temperature changes required, but this explanation is improbable for several reasons. In the first place, easily visible cavitation disappears at a fairly sharp point with increasing hydrostatic pressure, and beyond this point no acceleration occurs. This is an indication that the formation of bubbles which contain gas, and do not collapse readily, is the cause of acceleration. Again, many reactions are accelerated only when certain dissolved gases are cavitated, and are unaffected by the cavitation of others. Finally, sonic cavitation is in general almost noiseless, whereas the bubble collapse which produces high pressures is accompanied by a rattling sound.

A more attractive explanation has been suggested by **Marinesco (150)** who has ingeniously measured the surface temperatures of bubbles by determining whether explosives detonate when immersed in liquids which do not wet them. He finds that explosives with detonation temperatures below 230°C detonate, whereas those with higher detonation temperatures do not. The consistency of his remarks make it appear unlikely that resonance phenomena are present, and indicates that small regions of very high temperature exist in the liquid because of the presence of cavitated bubbles.

An alternative suggestion results from the computations of **Smith (185)** which show that enormous pressures are built up in the neighborhood of bubbles which are vibrating at their resonance frequencies. This will occur when the frequency of the sound wave is equal to a frequency determined by the diameter, surface tension, and gas pressure of the bubble. A sharp dependence on the acoustic frequency is of course entailed, after the manner of all resonance phenomena, and the explanation fails in the audible range because the dimensions of the resonant bubble become impossibly large.

Attention should be given in this connection to a paper by **Smith (185)** who investigated the pulsation vibrations of small gas bubbles under the action of alternating sound pressure. When their dimensions have a certain value, the bubbles vibrate in resonance, and the effect being that the local mechanical stresses in the

liquid may rise to 15,000 times the hydrostatic pressure. The resonance frequency of the gas bubbles depends on their radius, on the hydrostatic pressure and density of the liquid, on the ratio of the specific heats of gases, and on the surface tension between the gas and the liquid. It is not improbable that the chemical reactions are in part conditioned by these great concentrations of energy.

Some of these explanations provide regions in the liquid where the temperature is far higher than the average, and consequently they are perhaps sufficient to account for the acceleration of reactions which are already in progress. None can account, however, for luminescence, nor for the formation of hydrogen peroxide from oxygen and water which appears to be the basis for the acceleration of most oxidation reactions.

Therefore, it appears necessary to postulate a ballo-electrical mechanism in order to obtain sufficient energy. Just as the spraying of a liquid in air produces charged drops, the spraying of holes in a liquid, which is cavitation, must produce charged particles. In search for this effect, Richards ⁽¹⁶¹⁾ investigated the electrical potentials in a liquid which was forced into strong cavitation by driving it through a constriction in a wide tube with high hydrostatic pressure. Considerable random variations in potential were found in the region which was visibly cavitating, and none in other parts of the liquid which were flowing equally rapidly. It appears possible, therefore, that over distances comparable to molecular

dimensions, electrical potentials of the order of magnitude necessary to produce chemical reaction may be generated by cavitation. Apparently the first to appreciate this was Föttinger (30). A somewhat similar mechanism was suggested by Beuthe (23), who considered the origin of the charge frictional, and by Levsin and Kzevkin in connection with luminescence (122).

Frenkel (83) also states ultrasonic vibrations produce rupture cavitation leading to lens-shaped bubbles in which strong electrical forces come into play. It is stated that these electrical forces produce the observed chemical reactions.

Problems Encountered With Cavitation. In a paper by Pease and Blinks (148) it is shown that in general, the literature on cavitation and bubble formation presents a very confusing picture. Doring (86), Furth (90), Piccard (149), and Harvey (98) et al have "indicated that cavitation and bubble formation cannot be accounted for on the basis of random thermal movements in homogeneous solutions unless relatively enormous superheating, supersaturation, or negative tension is established. Most experimental work including that with supersonic vibrations suggests that cavitation and bubble formation require no great driving force." Much of the confusion has resulted because it has not been generally realized that there are two distinct problems. One concerns the nature and stability of gas masses which persist in fluids and on surfaces, and can and do act as nuclei for cavitation and bubble formation. When nuclei are

present, bubbles can be expected when the driving forces are very low. The other problem deals with cavitation and consequent bubble formation in the absence of any preexisting gas phase."

Harvey et al has demonstrated experimentally that the most commonly observed instances of cavitation and bubbling depend upon the presence of gas nuclei. In their experimentation they took a sample of water in a glass tube and subjected it to high hydrostatic pressure in order to force all preexisting gas masses into solution and thus have a system entirely devoid of gas nuclei. Water treated in this manner has unusual properties. It could be heated above 200°C without bursting into vapor. When the water was subjected to ultrasonic irradiation no cavitation occurred and no bubbles arise. If the glass tube containing the water was exhausted to the vapor pressure of water, moderate mechanical knocks had no effect and only a very severe blow causes bubbles to form.

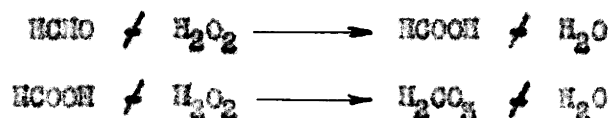
Harvey and his workers "deduced that a bubble nucleus is a gas mass trapped in a crack or depression on a hydrophobic surface. As a consequence, it can have a negative surface curvature (concave) at the fluid interface. Then surface tension will always tend to sustain or enlarge the gas mass, and a true equilibrium state can exist so that the nucleus can persist indefinitely. Thus dust particles and container walls are a potential source of nuclei which will almost invariably be present unless special precautions are taken." True cavitation should and could be studied with this potential source of serious confusion eliminated.

The basic findings of Pease and Blinks (148) is that certain types of stable solid surfaces are essential prerequisites for easy cavitation in the absence of gas nuclei. They believed they caused cavitation by literally starting a tear where no gas phase existed before. It was presumed that the tensions applied as driving forces were small (a few atmospheres at most). Thus any tear must have started at a very weak locus where the intermolecular forces momentarily approached zero. There only, fluid molecules momentarily can escape the attraction of fixed molecules which are unable to follow their movements. Conversely, in the body of any fluid, or at such solid-liquid interfaces where the attractive forces greatly exceed van der Waals forces, molecules are unable to separate sufficiently far to get out of one another's attractive spheres even momentarily, and large forces must be applied to initiate a tear.

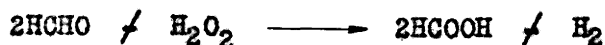
II. The Action Of Hydrogen Peroxide Upon Ethyl Alcohol

Anomalies In Literature. Fry and Payne (89) point out that:

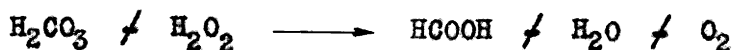
"Some perplexing anomalies are found in the reactions of hydrogen peroxide with simple compounds. For instance, as naturally expected, formaldehyde is directly oxidised to formic acid and the latter in turn to carbonic acid, thus



but hydrogen peroxide may, on the one hand, oxidize formaldehyde to formic acid with the liberation of hydrogen



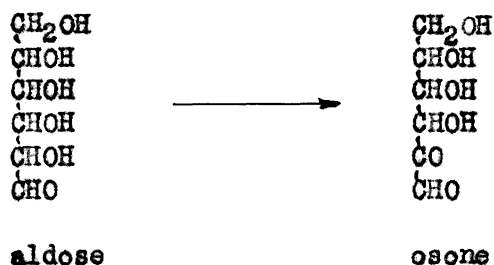
while on the other hand it will reduce carbonic acid to formic acid with the liberation of oxygen



Since hydrogen peroxide may thus react either as an oxidizing agent or as a reducing agent, and in some instances in both capacities concurrently, it is not surprising to find in the literature many conflicting reports as to the exact character of its reactions."

Mellor (134) states that hydrogen peroxide oxidizes many organic compounds, particularly in the presence of an inorganic salt as a catalytic agent. He states that hydrogen peroxide converts sugars into "ozones," and benzene into phenol in the presence of ferrous sulfate; the monohydric alcohols are not attacked, but the polyhydric alcohols are oxidized to the corresponding aldehydes, particularly in the presence of ferrous sulfate.

It is believed Mellor misquoted the literature in stating that hydrogen peroxide converts sugars into "ozones". What Mellor probably meant was osones which may be obtained from aldoses:



Kultyvgin and Sokolova (115) report that Mohr's salt in the presence of hydrogen peroxide can oxidize completely to carbon dioxide such organic compounds as sugars, lower fatty acids, hydroxy acids, and dicarboxylic acids. Simple alcohols and long chain fatty acids were not oxidized to carbon dioxide.

Rosenthaler (171) has found contrary to the statements of other investigators that the monoatomic alcohols from methyl to amyl are oxidized by ferrous sulfate and hydrogen peroxide.

Woodard and Pickles (209) found that mixtures of ethyl alcohol and hydrogen peroxide (10 volume) dispensed and stored under certain conditions, gave rise to yields of acetic acid and acetyl peroxide possessing clinical significance in the treatment of otitis. The residual peroxide content of the mixture was shown to be less than that of corresponding solutions of peroxide stored separately. To avoid the formation of undesirable oxidation products and also maintain maximum antiseptic value, mixtures of this type when ordered for long periods should always be dispensed separately.

Constitution Of Monohydric Alcohols. To understand more fully the problem of this investigation, monohydric alcohols should be briefly discussed. These alcohols may be regarded as paraffins (21), in the molecules of which one or more hydrogen atoms have been replaced by one or more univalent hydroxyl groups.

In the molecule of a monohydric alcohol, one of the hydrogen atoms plays a part different from that of the others. It is replaceable by metals such as sodium and potassium, and by acid

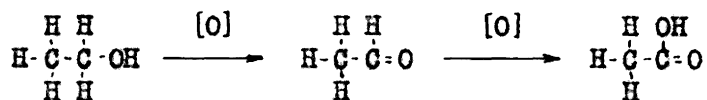
radicals, while the other hydrogen atoms of the alcohol remain unchanged (21). This replaceable hydrogen atom is called the "typical" or "extra-radical" hydrogen atom. It is not joined directly to the carbon atom, but through the oxygen one -- a conclusion which is confirmed by the formation of alcohols by the action of alkalies on monohalogen derivatives of the paraffins. The alcohols therefore contain a hydroxyl group, OH, and their general constitutional formula is $(C_nH_{2n-1}) \cdot OH$.

According to this theory (21), this hydroxyl can either replace an atom of hydrogen in a methyl group which forms an alcohol containing the group $\cdot CH_2OH$ or it can replace the hydrogen of a CH_2 group in a hydrocarbon, so that the resulting compound contains the group $\cdot CH \cdot OH$ -- the carbon being joined to the two other carbon atoms. It is also possible that in a hydrocarbon with a branching carbon chain, the hydrogen of a methine group CH may be replaced by hydroxyl, when the resulting alcohol would contain the group $\cdot C \cdot OH$, in which one carbon atom is joined to three others.

It may now be seen that the group $\cdot C \begin{array}{l} \text{H}_2 \\ \text{O} \cdot \text{H} \end{array}$ can, by further oxidation, be transformed into $\cdot C \begin{array}{l} \text{O} \\ \text{O} \cdot \text{H} \end{array}$. The latter, which is termed carboxyl, is contained in the acids $C_nH_{2n}O_2$, or $C_{n-1}H_{2n-1}COOH$, which is formed by the oxidation of the primary alcohols. Consequently, it is the primary alcohols which contain the group $\cdot CH_2 \cdot OH$.

Oxidation Of Ethyl Alcohol. Methyl, ethyl, and many higher alcohols are highly susceptible to oxidation (75), and are attacked readily by chromic acid in acetic acid and by potassium dichromate

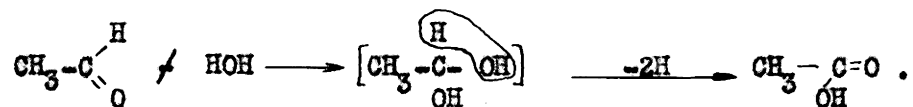
or potassium permanganate in acid solution. Since methane and ethane are fully resistant to the same reagents, it can be concluded that the presence of oxygen in a molecule makes the substance more susceptible to further oxidation. In ethyl alcohol, one of the two carbon atoms is linked to oxygen, and hence is in an already oxidized condition, while the other is joined to hydrogen and carbon and corresponds to the carbon atoms of the inert ethane, and it is in line with the above conclusion that oxidizing agents attack the molecule at the former, rather than the latter position. The initial oxidation product is



acetaldehyde, and this on further oxidation is attacked in the already oxidized part of the molecule and yields acetic acid as an end product resistant to further attack.

From a theoretical point of view, the first step in the overall process can be regarded as a dehydrogenation, rather than an oxidation, involving the elimination of a hydroxylic hydrogen together with a hydrogen of the hydroxylated carbon atom, with the direct establishment of a carbon-oxygen double bond. The reagent employed to effect the reaction is regarded not as an oxidizing agent, but as a hydrogen acceptor. The second step leading to acetic acid also can be interpreted as a dehydrogenation if it is supposed that the

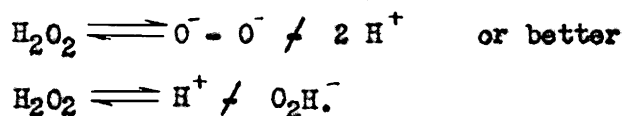
reaction proceeds through the transient formation of an unstable hydrate of acetaldehyde:



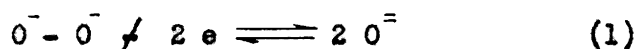
Hydrogen Peroxide As An Oxidizing Agent. As an oxidizing agent, hydrogen peroxide is characterized by the distinct advantage of producing only water as a by-product. This is of great significance in the manufacture of dyestuffs, pharmaceuticals, and food chemicals where metallic impurities resulting from oxidizing agents are often deleterious to the final product.

Hydrogen peroxide can act in both oxidizing and reducing fashions as already shown. In the course of time a large number of theories have been developed in explanation of these peculiar relations, but only a few will be mentioned here.

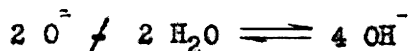
(a) Electrochemical Theory. It is a familiar fact that hydrogen peroxide is a weak acid:



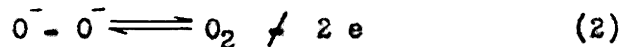
According to Fredenhagen's (82) electrochemical theory -- "if the O-O anion is reduced to two oxygen ions by taking up two electrons, the peroxide acts in an oxidizing manner:



The oxygen ions now react with water to form hydroxyl ions:

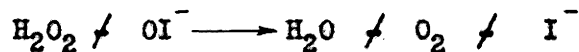


On the contrary, the peroxide acts as a reducing agent if the $O^- - O^-$ ion gives up its charge to form gaseous oxygen:

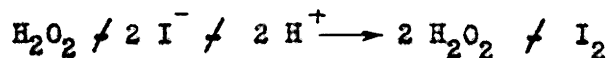


The reducing action is therefore connected with the evolution of free oxygen as in permanganate titrations.

In general, the peroxide inclines more toward reducing action in alkaline solution and more toward oxidizing action in acid solution. For example, hypiodite and also hypobromite are reduced ⁽⁸²⁾ by peroxide in alkaline medium:



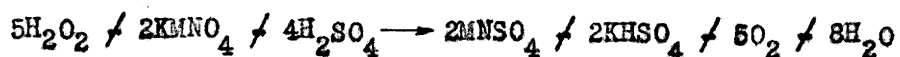
In acid solution, on the other hand, it oxidizes iodide to iodine:



Ferricyanide also undergoes reduction to ferrocyanide by hydrogen peroxide in alkaline solution; conversely, acidified ferrocyanide solution is oxidized to ferricyanide. The great influence of hydrogen-ion concentration is explained by the fact that the concentration of oxygen ions (equ. 1) is much greater in alkaline solution than in acid. The peroxide is converted into O^- and then into OH^- by a reducing action.

In acid solution the oxidation finds much less resistance because the O^- or OH^- ions are continually removed. On the contrary, peroxide in alkaline solution is able to react more according to equation 2. That hydrogen peroxide can in addition act also as a reducing agent toward strong oxidizing agents even in acid

solution follows from its familiar reaction with potassium permanganate." This reaction may be expressed by the equation:



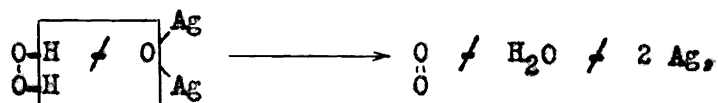
(b) Bancroft and Murphy (5) take the argument that "if hydrogen peroxide decomposed, as is usually assumed, according to the equation $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} \nearrow \text{O}$, it would be setting free nascent oxygen which is, next to fluorine, the most powerful oxidizing agent that we have at ordinary temperatures." Their work "was started with the idea that one could do chemical electrolyses with hydrogen peroxide nearly as well as with fluorine. That view was given up when it was found experimentally that hydrogen peroxide is a rather weak oxidizing agent since what is first evolved is $\text{O}\cdot\text{O}$ and not O ."

At this point it is interesting to note that other investigators have found hydrogen peroxide to be a "strong" oxidizing agent. Thorne and Roberts (196) report that chemically, hydrogen peroxide is a "strong" oxidizing agent, but as such acts best in alkaline solution. It converts the hydroxides of bivalent iron and cobalt into the trivalent, and that of manganese into the quadrivalent form, while alkaline chromic salts are oxidised to the chromate and changes like that of ferro- and cobalto-potassium cyanide to the higher complex compounds take place very rapidly with hydrogen peroxide.

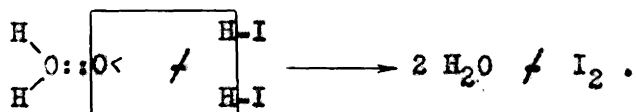
Shanley and Greenspan (182) while discussing highly concentrated hydrogen peroxide with representative organic

substances show oxidation results which were in the range of no reaction to 100 per cent efficiency with a tendency toward overoxidation in the case of ethyl alcohol.

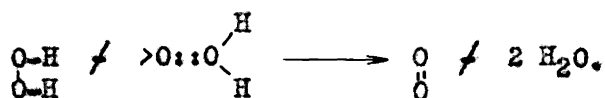
(c) In a theory on the structure of hydrogen peroxide and the mechanism of its reactions, Raikow (152) "proposes that hydrogen peroxide is an allotropic mixture of two tautomers: the symmetrical compound $\text{O}-\text{H}$, which he calls 'hydrogen pseudo peroxide,' and the unsymmetrical compound $\text{>O}::\text{O}\begin{matrix} \text{H} \\ \text{H} \end{matrix}$, which he calls 'hydrogen peroxide.' The mixture is called hydrogen dioxide, and consists principally of the pseudo compound, with only a very small amount of the peroxide. This explains the vigorous reducing action, written as



and the mild oxidizing action



Spontaneous decomposition of hydrogen peroxide is due to interaction of these two forms, as follows:



It proceeds slowly because of the small amount of peroxide."

III. EXPERIMENTAL

A. Purpose And Plan

The purpose of this investigation is to study the effect of ultrasonic irradiation on ethyl alcohol-hydrogen peroxide-water mixtures.

The plan of procedure used in this investigation was to consider and limit in so far as practicable the numerous variables involved, and then to subject a definite mixture of ethyl alcohol-hydrogen peroxide-water to ultrasonic irradiation.

Quantitative determinations of the pH, "acid content" by titration with an alkali, hydrogen peroxide content, and aldehyde content were made prior to ultrasonic irradiation and subsequent to ultrasonic irradiation. In this way, relative changes caused by the ultrasonic irradiation could be determined.

Variables considered in this investigation were:

- a. Limitations of the ultrasonic oscillator such as frequencies available, and the amount of power to be applied to the quartz crystals.
- b. Adjustment of impedance matching unit.
- c. Level of transformer oil above quartz crystal in transducer.
- d. Temperature of transformer oil in transducer.
- e. Temperature of ethyl alcohol-hydrogen peroxide-water mixture.
- f. Type of container for the ethyl alcohol-hydrogen peroxide-water mixture.
- g. Position of container in transducer.
- h. Weight of ethyl alcohol in mixture to be irradiated.
- i. Weight of hydrogen peroxide in mixture to be irradiated.

- j. Volume of ethyl alcohol-hydrogen peroxide-water mixture to be irradiated.
- k. Period of time of ultrasonic irradiation on ethyl alcohol-hydrogen peroxide-water mixture.
- l. Chemical reactions assumed to take place.
- m. Known analytical procedures.
- n. Purity of reagents.

B. Materials

The materials used in this investigation were:

Acid, Acetic. CP glacial. Lot number 5246. J. T. Baker

Chemical Company, Phillipsburg, N. J.

Acid, Sulfuric. CP. Sp gr at 60°F minimum 1.84. Eimer and Amend, New York, N. Y.

Alcohol, Ethyl. Absolute. Quality and source unknown.

Prepared by the Virginia Polytechnic Institute Chemistry Department by refluxing with calcium oxide.

Alcohol, Ethyl. USP, 95 per cent. Serial number 171457.

U. S. Industrial Chemicals, Inc., Baltimore, Md.

Specifications: "Acidity: Free acid as acetic acid, not more than 0.0014 gm per 100 cc.

Color: Water-white.

Non-volatile Matter: Not more than 0.0025 gm per 100 cc.

Odor: Free from foreign odors when tested at high or low proof.

Purity: Not less than 95 per cent ethyl alcohol by volume.

Reducing Substances: Not less than 45 minutes permanganate time.

Specific Gravity: At 60°/60° F - not more than 0.8158."

Alcohol, Ethyl. USP, absolute grade. Serial number 176703.

U. S. Industrial Chemicals, Inc., Baltimore, Md.

Specifications: "Acidity: Free acid as acetic, not more than 0.0014 gm per 100 cc.

Color: Water-white.

Non-Volatile Matter: Not more than 0.0025 gm per 100 cc.

Odor: Free from foreign odors when tested at high or low proof.

Purity: Not less than 99.9 per cent ethyl alcohol by volume.

Reducing Substances: Not less than 25 minutes permanganate time.

Specific Gravity: At 60°/60° F - not more than 0.794."

Alcohol, Methyl. Baker and Adamson synthetic grade. Code 1214. Lot number C 205 J. General Chemical Co., New York, N. Y.

Aldehyde Ammonia. CP crystal. Lot number 472365. Eimer and Amend, New York, N. Y.

Ammonium Hydroxide. CP. Lot number E 212003. Sp gr 0.90, minimum ammonia 28 per cent. General Chemical Co., New York, N. Y.

Barium Chloride. CP. Crystal. Lot number 50 C. General Chemical Co., New York, N. Y.

Buffer Solution. Concentrated. Lot number 171009. National Technical Laboratories, South Pasadena, California.

Specifications: 1 volume concentrated buffer with 49 volumes distilled water gives pH = 7.07 \pm 0.04 at 25°C.

Calcium Carbonate. CP powder. Lot number 8243. J. T. Baker Chemical Company, Phillipsburg, N. J.

Diethyl Ether. CP anhydrous. Lot number 477353. Eimer and Amend, New York, N. Y.

Ferric Chloride. CP, lump. Lot number 103046. J. T. Baker Chemical Company, Phillipsburg, N. J.

Fuchsin Basic. Total dye content 91 per cent. Certification number NF 54. National Aniline Division, Allied Chemical and Dye Corporation, New York, N. Y.

Fuchsin, Basic. Total dye content 77 per cent. Certification number NF 23. National Aniline & Chemical Co., Inc., New York, N. Y.

Fuchsin, Basic. Lot number 370724. The Coleman & Bell Co., Norwood, O.

Hydrogen Peroxide. Superczol, 30 per cent CP. Merck and Co., Rahway, N. J.

Lot number 40908 and Lot number 43357:

<u>Specifications:</u>	Assay: Minimum 29 % H ₂ O ₂
Non-Volatile	0.050 % Phosphate (PO ₄) 0.005 %
Free acid (as H ₂ SO ₄)	0.10 % Sulfate (SO ₄) 0.025 %
Chloride (Cl)	0.001 %

Iodine. CP. Lot number 480119. Eimer and Amend, New York, N. Y.

Lanthanum Nitrate. CP. Lot number 464002. Eimer and Amend, New York, N. Y.

Metaphenylenediamine Hydrochloride. CP. Lot number 474552.

Eimer and Amend, New York, N. Y.

Phenolphthalein. CP. Lot number 462166. Eimer and Amend,

New York, N. Y.

Potassium Hydrogen Fththalate. CP. Lot number 470847. Eimer

and Amend, New York, N. Y.

Potassium Iodide. CP, crystal. Lot number 470145. Eimer and

Amend, New York, N. Y.

Potassium Permanganate. CP. Lot number 40218. Merck and

Company, Inc., Rahway, N. J.

Sodium Acetate. CP, crystal. Lot number 22546. J. T. Baker

Chemical Company, Phillipsburg, N. J.

Sodium Bisulfite. CP, granular. Lot number 122347. J. T.

Baker Chemical Company, Phillipsburg, N. J.

Sodium Hydroxide. CP, pellets. Lot number 102645. J. T. Baker

Chemical Company, Phillipsburg, N. J.

Sodium Oxalate. CP, special powder. Lot number 21540. J. T.

Baker Chemical Company, Phillipsburg, N. J.

Sodium Sulfite. CP, anhydrous. Lot number 91345. J. T. Baker

Chemical Company, Phillipsburg, N. J.

Sulfur Dioxide Cubes. Eimer and Amend, New York, N. Y.

Transformer Oil. Sunoco. Eimer and Amend, New York, N. Y.

Water. Double distilled. Prepared by adding potassium

permanganate to distilled water and then redistilling.

C. Apparatus

The equipment and apparatus used in this investigation was:

1. Balance, Analytical. Chainomatic, dampened, maximum weight 201.1 grams. Sensitivity 0.001 grams. Serial number 11 G 3039. Seederer-Kohlbusch, Inc., Jersey City, N. J.

Weights, Analytical. Serial number 4 D 2238. Seederer-Kohlbusch, Inc., Jersey City, N. J.

2. Balance, Triple Beam. Maximum weighing 610 grams. Rated sensitivity 1/10 gram. The Chemical Rubber Co., Cleveland, O.

3. Colorimeter, Klett-Summerson Photoelectric. Patent number 2193427-1940. Number 3366, 115 v. Klett Manufacturing Company, New York, N. Y. Green filter number 54 with approximate spectral range of 500-570 millimicrons was used with this instrument.

Operating instructions, wiring diagram, and other pertinent information may be had by referring to the manual supplied with the instrument.

4. Cooler, External For Transformer Oil In Ultrasonicator Transducing Unit.

a. Materials used in constructing cooler:

(1) Pipe and fittings.

One 1/4 x 2 inch galvanized iron nipple.

One 1/4 inch brass globe valve.

Four 3/8 inch brass adaptors, copper to iron.

Two 3/8 inch galvanized iron couplings.

Two 3/8 inch galvanized iron tees.

Two 3/8 inch galvanized iron nipples.

Two 3/8 inch thermometer well caps with 1/4 by 4 inch copper tubing.

Two 3/8 x 1 1/2 inch galvanized iron nipples.

Two 3/4 inch thermometer well caps with 1/4 x 4 inch copper tubing.

Three 1 inch galvanized iron couplings.

One 1 inch galvanized iron street ell.

Four 1 x 2 inch galvanized iron nipples.

Two 1 x 3/4 inch galvanized iron bushings.

One 3/4 x 2 inch galvanized iron nipple.

One 3/4 x 3 inch galvanized iron nipple.

Two 1 inch galvanized iron union.

Six 1 inch galvanized iron ells.

Two 1 inch galvanized iron tees.

One 1 inch galvanized iron plug.

Twenty-seven feet four inches 1 inch galvanized iron pipe.

One 1 inch brass needle valve.

(2) Copper tubing.

Seventy feet 3/8 inch copper tubing.

(3) Glass tubing.

Fifteen inches glass tubing (8 mm ID, 11 mm OD).

(4) Tygon tubing.

Six inches (10 mm ID, 13 mm OD).

(5) Thermometers.

Four 8 inch stem Weston Metal Thermometers (0° -180°F).

(6) Angle iron frame to support oil pump and electric motor

with the following dimensions:

7½ inches (width)

22 inches (length)

4½ inches (height)

(7) Angle iron frame to support external cooler with the follow-

ing dimensions:

14½ inches (width)

14½ inches (length)

4-3/4 inches (height)

(8) Motor, Electric with cord and male plug. Century motor.

Capacitor single phase. Model CSH-65L-RHK4-3FA. 1/4 Hp, 115/230 v,

60 c, 1750 rpm, 4/2 amps. Serial number AC 1. Century Electric

Company, St. Louis, Mo.

(9) Pump. Positive displacement gear. 8 gallon per minute

capacity. Number ROA 203, FIG 5130 3/8.

(10) Filter. Fram Replacement Cartridge number FB½ with

adaptors. Fram Corporation, Providence, R. I.

(11) Pulleys. One 4" x 3½" x 2½" aluminum pulley. One 6½ inch aluminum pulley.

(12) Belting. One 44 inch V-belt.

(13) One sheet iron drum (13½ x 24 inches).

(14) One sheet iron plate for drum top ($13\frac{1}{2}$ inches diameter by 24 gauge).

(15) Miscellaneous:

Eight $1/4$ x 1 inch iron stove bolts with nuts and washers for fastening pump and electric motor to angle iron frame.

One pint outside gray deck paint.

One 2 inch paint brush.

One laboratory ring stand.

Two $1/4$ x 4 inch lag bolts to fasten ring stand to wall.

Two laboratory clamp holders.

b. Design Calculations for the External Oil Cooling Unit.

(1) Initial Assumptions:

0.5 gallons per minute of oil to be pumped.

25 gallons per minute of water through 1 inch galvanized iron pipe to cooler.

Inlet temperature of oil to cooler is 22°C or 71.6°F .

Outlet temperature of oil from cooler is 20°C or 68.0°F .

Inlet temperature of water to cooler is 19°C or 66.2°F .

Outlet temperature of water from cooler is 19°C or 66.2°F . A negligible rise of temperature was assumed due to the flow of water assumed.

(2) Known Data:

Outside diameter of $3/8$ inch copper tubing is 0.375 inches.

Inside diameter of 3/8 inch copper tubing is 0.312 inches.

Average diameter of 3/8 inch copper tubing is 0.343 inches.

Wall thickness of 3/8 inch copper tubing is 0.063 inches.

Circumference of 3/8 inch copper tubing is 1.17 inches.

Outside surface area per foot of 3/8 inch copper tubing is 14.04 sq in.

Specific gravity of transformer oil at 33°C is 0.85.

Specific gravity of transformer oil at 25°C is 0.90.

Assumed specific gravity of transformer oil at 22°C is 0.90.

Assumed specific gravity of transformer oil at 37.8°C is 0.82.

Viscosity (Saybolt Universal) of transformer oil at 37.8°C is 55 seconds.

Specific heat of transformer oil is 0.445.

(3) Calculations:

(a) Conversion of Viscosities. Readings on Saybolt viscometer may be converted to absolute viscosities by the equation (4), $\frac{\mu}{s} = 0.22 \theta - \frac{180}{\theta}$, where μ = viscosity in centipoises; s = specific gravity; θ = Saybolt reading in seconds. Therefore, $\frac{\mu}{0.82} = 0.22 (55) - \frac{180}{55} = 7.24$ centipoises at 37.8°C.

On this basis, assume $\mu = 5$ centipoises at 20°C . Centipoises may be converted to $\text{lbs}/(\text{hr})(\text{ft})$ by multiplying by 2.54. Therefore, $5 \times 2.54 = 12.7 \text{ lbs}/(\text{hr})(\text{ft})$.

(b) Heat from Oil:

$$\text{Weight} = 0.5 \frac{\text{gal}}{\text{min}} \times 60 \frac{\text{min}}{\text{hr}} \times 8.345 \frac{\text{lbs}}{\text{gal}} \times 0.90$$

$$W = 225.3 \text{ lbs/hr}$$

$$q = Wc_p dt$$

$$q = 225.3 \times 0.445 (71.6 - 68)$$

$$q = 360.48 \text{ Btu/hr}$$

(c) Oil Flow:

$$\text{Inside diameter of tubing is } \frac{0.312 \text{ in}}{12 \text{ in/ft}} = 0.026 \text{ ft.}$$

$$\text{Rate of flow} = 0.5 \frac{\text{gal}}{\text{min}} \text{ or } \frac{0.5 \text{ gal/min}}{60 \text{ sec/min}} = 0.0083 \frac{\text{gal.}}{\text{sec}}$$

One gallon = 0.1337 cu ft. Therefore, $0.0083 \text{ gal/sec} \times 0.1337 \text{ cu ft/gal} = 0.0011 \text{ cu ft/min.}$

$$\text{Cross sectional area of tubing is } \frac{\pi D^2}{4} \text{ or } \frac{3.14(0.312/12)^2}{4} = 0.00053 \text{ sq ft.}$$

$$\text{Velocity} = \frac{q}{s} = \frac{\text{cu ft/sec}}{\text{sq ft}} = \frac{0.0011}{0.00053} = 2.08 \frac{\text{ft.}}{\text{sec}}$$

$$\text{Mass velocity, } G = \rho V \text{ where } G = \frac{\text{lbs}}{(\text{hr})(\text{ft}^2)} ;$$

ρ = density in $\text{lb}/\text{cu ft}$; V = velocity in ft/hr . Therefore,

$$G = 2.08 \text{ ft/sec} \times 3600 \text{ sec/hr} \times 0.90 \times 62.4 \text{ cu ft}$$

$$G = 420726 \text{ lb}/(\text{hr})(\text{sq ft}).$$

(d) Reynold's number, $Re = DG/\mu$ where $D =$ inside diameter of tubing in feet; $G =$ mass velocity in $\text{lbs}/(\text{hr}) (\text{ft})^2$; $\mu =$ viscosity in $\text{lbs}/(\text{hr}) (\text{ft})$.

$Re = \frac{0.026 \times 420726}{12.7} = \frac{10958.8}{12.7} = 860$. Re is less than 2100, so the oil flow is viscous.

(e) Flow of Water in Cooler. It was assumed that 25 gallons per minute of water flowed through a one inch galvanized iron pipe to the cylindrical sheet iron cooler. Therefore, $25 \times 0.1137 = 3.54$ cubic feet per minute flow.

The dimensions of the cylindrical cooler was 13.5 inches in diameter and 24 inches in length or height since the cylinder was placed in position on one of its ends. The volume of the cooler is $\frac{1}{4} \pi D^2 \times h = \frac{3.14 \times (13.5/12)^2 \times 24}{4} = 1.96$ cu ft.

The theoretical height of the cylinder required for 3.34 cu ft of water may be determined by the relation $\frac{1}{4} D^2 \times h =$ cu ft. Expressed arithmetically this is $\frac{3.14 \times (13.5/12)^2 \times h}{4} = 3.34$ cu ft. Therefore, h equals 3.4 feet which is the theoretical height of the cylindrical cooler to hold 3.34 cu ft of water. If 3.34 cu ft of water fills this theoretical cylinder in one minute then the flow is 3.4 ft/min or 0.056 ft/sec.

(f) Film Transfer Rates. By examining data given by Nelson, (138) the water film transfer rate was assumed to be 50 Btu/(sq ft) (hr) ($^{\circ}F$).

Using other data by Nelson, (137) the film transfer rate for oil was estimated to be 100 Btu/(sq ft) (hr) (°F).

Nelson (136) states that the thermal conductivity for copper at 70°F is 227 Btu/(°F diff) (sq ft) (hr) (ft).

(g) Overall coefficient based on outside area:

$$U = \frac{1}{\frac{D_2}{D_1 h_1} + \frac{D_2 L}{D_{av} k} + \frac{1}{h_2}} \quad \text{where}$$

U = Overall coefficient in Btu/(hr) (sq ft) (°F).

h₁ = Film coefficient in Btu/(hr) (sq ft) (°F) on hot side.

h₂ = Film coefficient in Btu/(hr) (sq ft) (°F) on cold side.

D₁ = Diameter in feet on hot side.

D₂ = Diameter in feet on cold side.

k = Thermal conductivity in Btu/(°F diff) (sq ft) (hr) (ft).

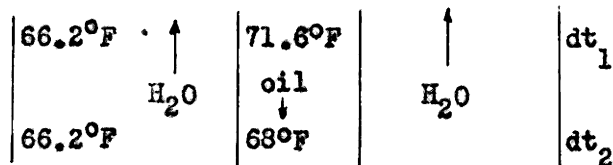
L = Wall thickness in feet.

$$U = \frac{1}{\frac{\frac{0.375}{12}}{\frac{0.312 \times 100}{12}} + \frac{\frac{0.375 \times 0.063}{12}}{\frac{0.343 \times 227}{12}} + \frac{1}{50}}$$

$$U = \frac{1}{0.012 + 0 + 0.02} = 31$$

(h) Mean Temperature Difference. The rise in temperature of exit water from the cooler is negligible due to the diameter of the cooler and the flow of water.

Thermal conditions in cooler:



$$dt_1 = 71.6 - 66.2 = 5.4 \quad ; \quad dt_2 = 68.0 - 66.2 = 1.8$$

$$dt_m = \frac{5.4 - 1.8}{2.3 \log 5.4/1.8} = 3.6/2.3 \log 3 = 3.3^\circ\text{F.}$$

$$q = UAdt; \quad 360 = 31(A)3.3; \quad A = 3.5 \text{ sq ft.}$$

(i) Length Of 3/8 Inch Copper Tubing Required.

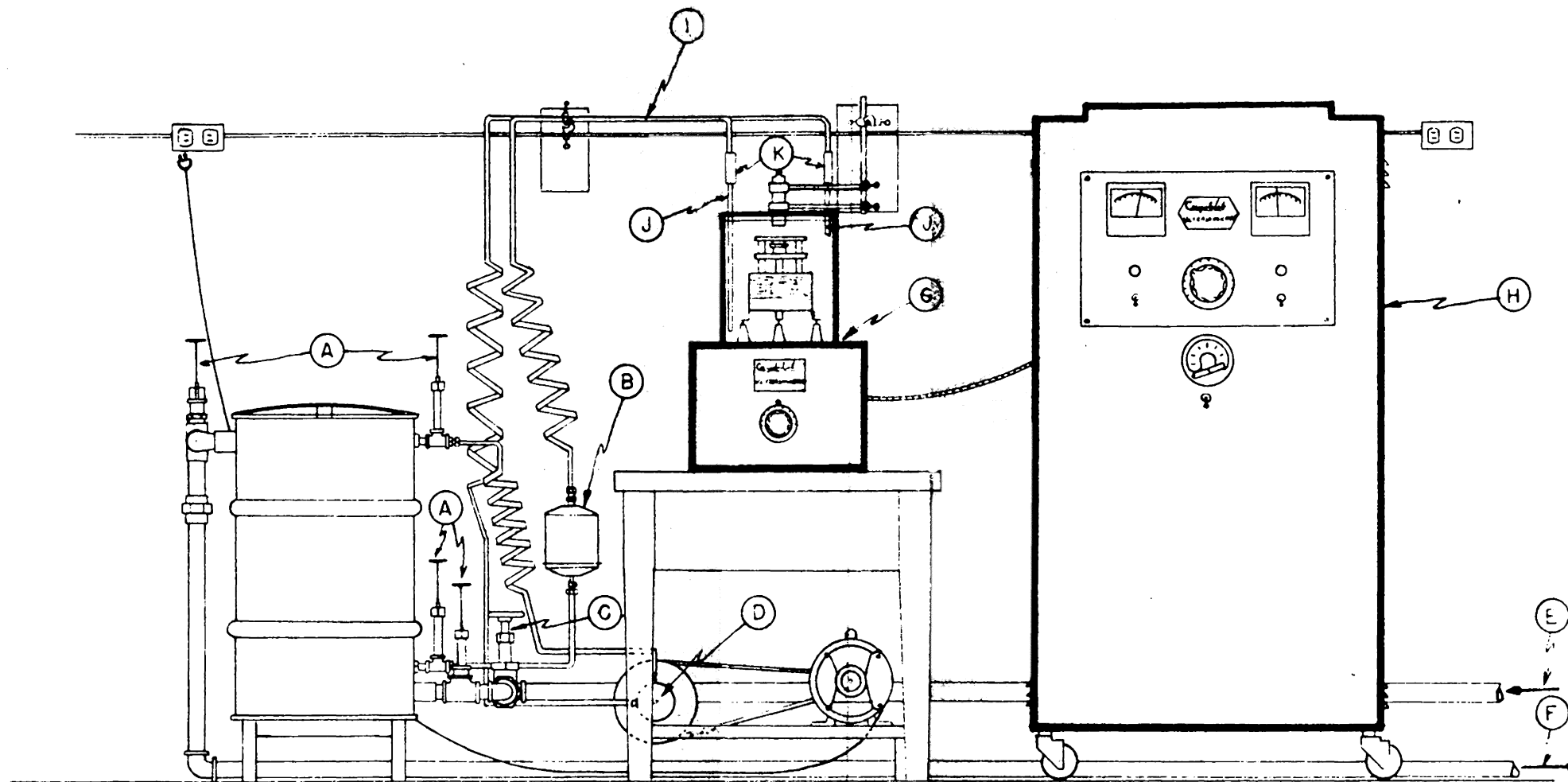
The outside surface area per foot of 3/8 inch copper tubing is 14.04 sq in. 3.5 sq ft of surface area are required for cooling the oil so this is 3.5 sq ft x 144 sq in/sq ft = 504 sq in. 504 sq in/14.04 sq in/ft = 36 feet of 3/8 inch copper tubing required.

A 10 per cent safety factor was added which is 4 feet of copper tubing. Therefore, 40 feet of 3/8 inch copper tubing was required for the desired cooling.

c. Figure 11 and figure 12 show the cooler and other major equipment in elevation.

5. Constant Temperature Bath (figure 13) for Development of Color in Acetaldehyde Determination. Equipment used was:

- One ringstand
- One 4 inch ring
- Two clamp holders
- One clamp



LEGEND

- (A) Weston Thermometer
- (B) Fram Filter
- (C) Water Regulating Valve
- (D) Gear Pump
- (E) Water Inlet
- (F) Water Outlet

- (G) Transducer
- (H) Radio Frequency Generator
- (I) Copper Tubing
- (J) Glass Tubing
- (K) Tygon Tubing

REVISIONS

DEPARTMENT OF CHEMICAL ENGINEERING
 VIRGINIA POLYTECHNIC INSTITUTE
 BLACKSBURG, VIRGINIA

EQUIPMENT LAYOUT

SCALE NONE
 DRAWN BY WCG 12-9-48
 TRACED BY WCG 12-9-48
 CHECKED BY FCV 12-17-48

FILE 535-48
 APPROVED BY FCV 12-17-48
 DRAWING NUMBER /
 FIGURE NUMBER //

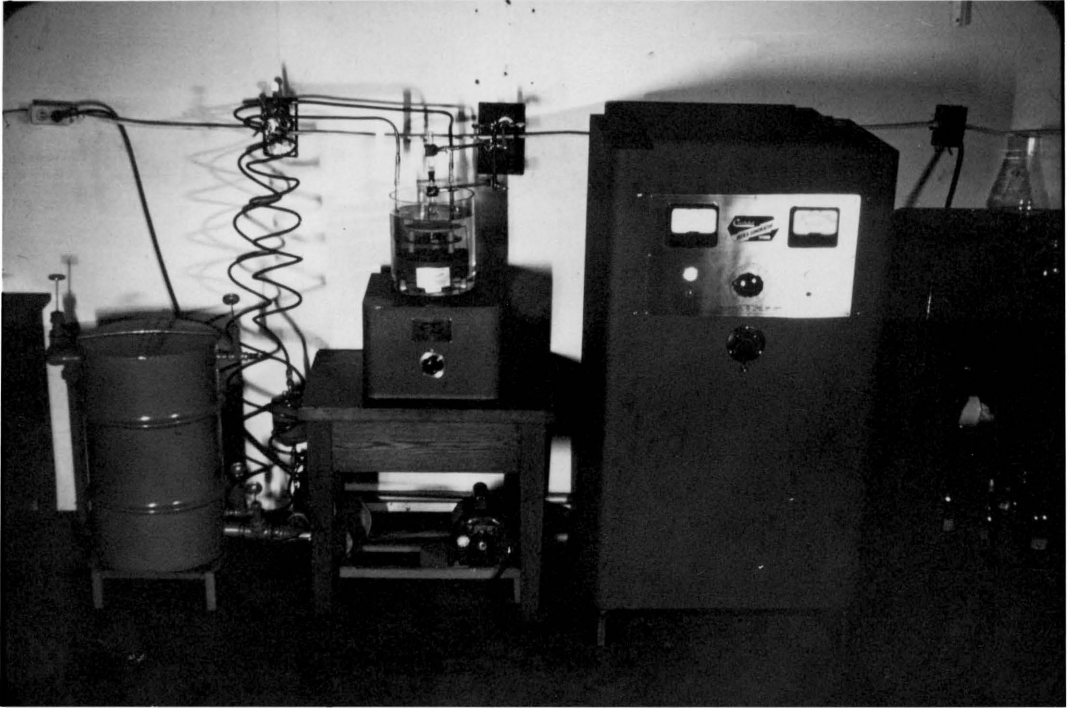


Figure 12

Elevation View of Equipment

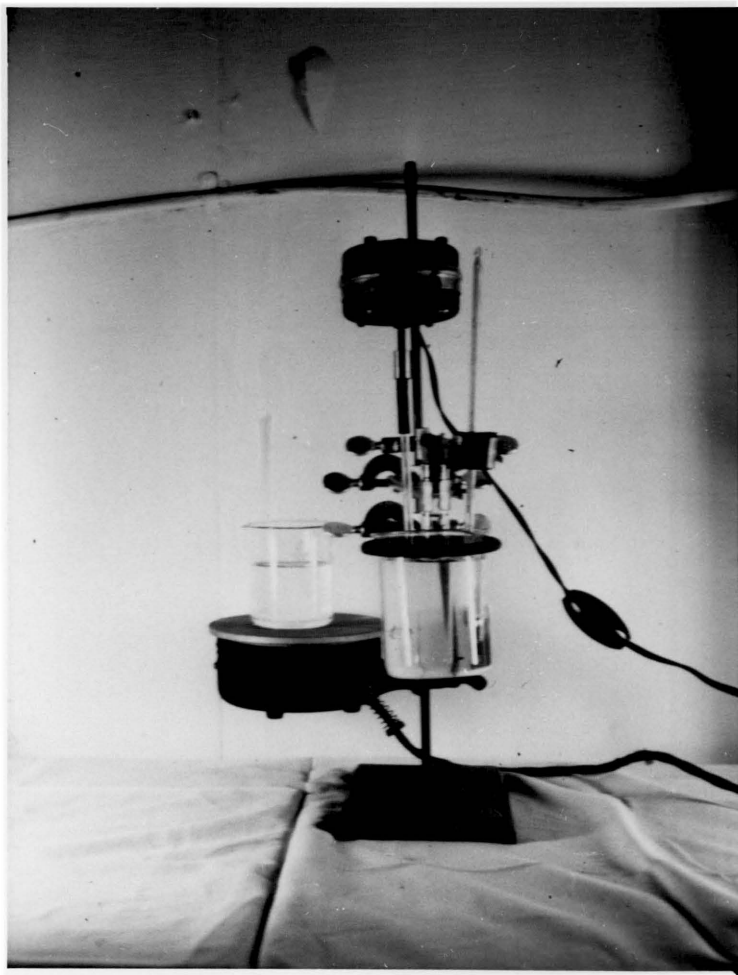


Figure 13

Constant Temperature Bath

One glass thermometer (-20°C to 110°C, Number 06411, Brothcom, N. Y.)

One 400 ml pyrex beaker

One laboratory stirrer fitted with glass rod for rotor, 115 v, 60 c, Eimer and Amend, New York, N.Y.

One electric heater. Autemp, 115 v AC only. Eimer and Amend, New York, N. Y.

One 300 ml pyrex beaker.

One No. 6 one hole rubber stopper

Six test tubes (25 mm x 150 mm OD)

Six No. 7 corks

One chronograph.

6. Laboratory Equipment. Equipment used was one 1000 ml beaker, two 600 ml beakers, two 400 ml beakers, four 250 ml beakers, two 150 ml beakers, four 100 ml beakers, six 50 ml beakers, eighty glass beads, one buret brush, one test tube brush, one funnel brush, two buret clamps, two 50 ml burets, two microburets, three calcium chloride drying tubes, twelve clamps, twelve clamp holders, assorted corks and rubber stoppers, one vacuum desiccator, one calcium chloride desiccator, one box 12 cm Whatman No. 40 filter paper, two Fisher burners, three 2000 ml round bottom flasks, one 2000 ml erlenmeyer flask, one 1000 ml florence flask, one 1000 ml distilling flask, four 1000 ml volumetric flasks, four 500 ml volumetric flasks, twelve 100 ml volumetric flasks, twelve 50 ml volumetric flasks, one 65 mm diameter funnel, one 12 inch diameter funnel,

one wood funnel support, one 12 cm Buchner funnel, three 50 ml graduated cylinders, one 100 ml graduated cylinder, two 250 ml graduated cylinders, one mortar and pestle, assorted glass rods, twelve nessler tubes, one nessler tube rack, assorted pipets, two micro-pipets, one porcelain spot plate, tubing (glass, rubber, tygon), one 12 inch water bath with tripod, three pneumatic troughs, one 25 ml glass pycnometer, three reflux condensers, six ringstands, eight screw clamps, twenty four test tubes, two test tube racks, two glass traps, one thistle tube, one 25 ml weighing bottle, four wire gauze.

7. Laboratory Furniture. Tables, desks, chairs, etc.

8. Oven, Drying. Serial number 100-2761. Catalog number 1250. Temperature range 35 to 180°C, volts 110, cycles 60, watts 600, amps 5.5, phase 1, type A. Precision Scientific Co., Chicago, Ill.

9. pH Meter. Beckman Glass Electrode. Model H. Serial 2023, 115 v, 50-60 cycle. National Technical Laboratories, South Pasadena, California.

10. Table. Oak wood to support Ultrasonerator transducing unit. Dimensions: 20 inches wide, 25-3/4 inches long, 24 inches high.

11. Reaction vessel for ethyl alcohol-hydrogen peroxide-water mixture.

12. Refractometer, Spencer. Number 547. Spencer Lens Co., Buffalo, N. Y.

13. Ultrasonerator. Model number SL 520. Serial number 132. Manufactured by Crystal Research Laboratories, Inc., Hartford, Conn. For complete operating details, see instruction manual that accompanies equipment.

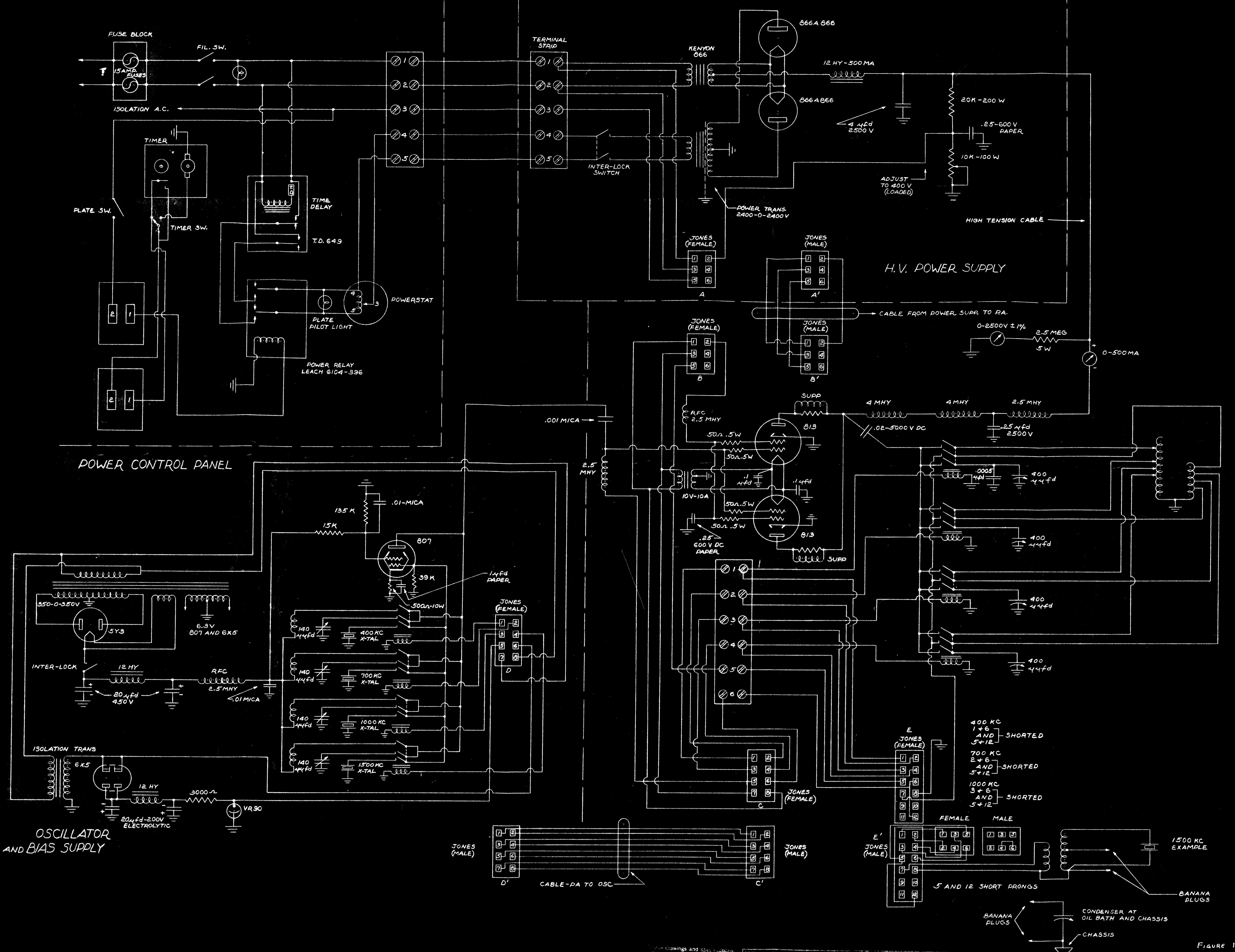
The wiring diagram is shown in figure 14. The interior of the radio frequency generator from the rear is shown in elevation view in figure 15. The ultrasonerator transducing crystal is shown in elevation view in figure 16 and figure 19.

14. Utilities such as heat, light, gas, water, steam, and electricity.

D. Method Of Procedure

Introduction. It was the original intention of this investigator to subject ethyl alcohol-water mixtures, into which air was being passed, to ultrasonic irradiation. It was expected that hydrogen peroxide could be produced to oxidize some of the ethyl alcohol to acetaldehyde and possibly to acetic acid.

However, after considering the literature review it was believed insufficient hydrogen peroxide would be produced to cause any relative change that could be detected by ordinary analytical procedures. This original idea was abandoned in favor of using 30 per cent hydrogen peroxide with the ethyl alcohol and water. This mixture was to be subjected to ultrasonic irradiation and qualitatively and quantitatively analyzed before and after irradiation.



These drawings and specifications are the property of Crystal Research Laboratories, Inc., Hawthorne, California, U.S.A., and shall not be reproduced or used as the basis for the manufacture or sale of apparatus, without permission.

NAME: ULTRA-SONORATOR
 DATE: JAN 10-4-46
 BY: L.H. WMAA
 ENGINEERING DEPARTMENT
 DRAWING NO. 4179

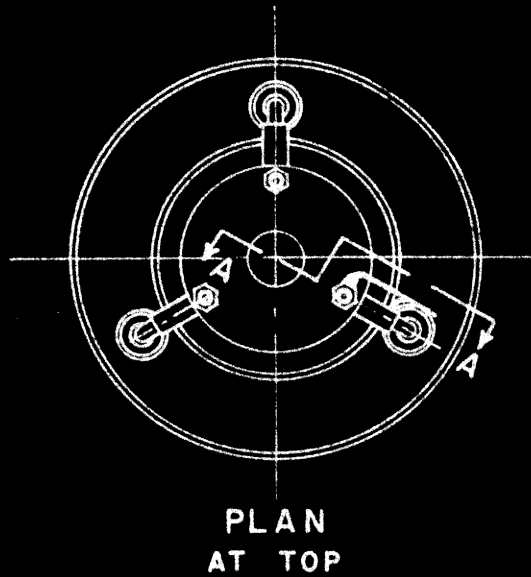
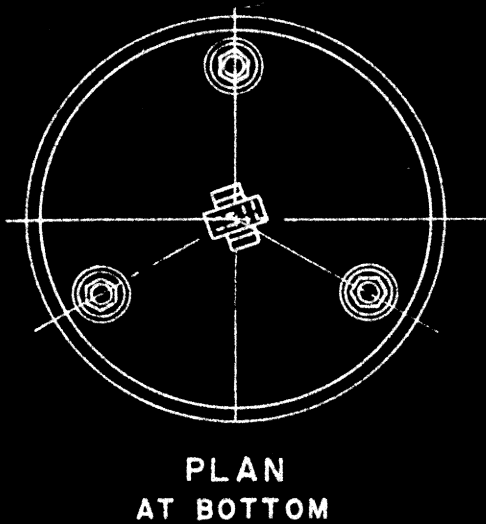
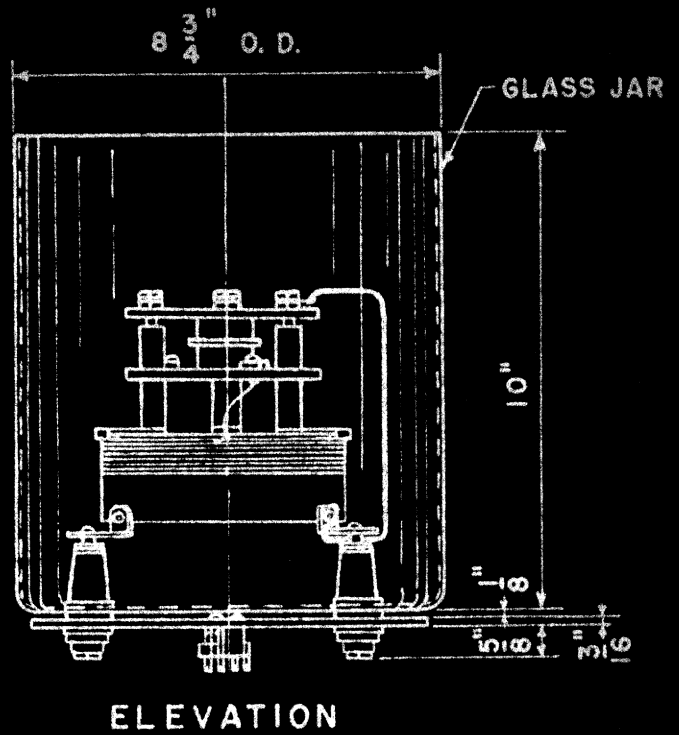
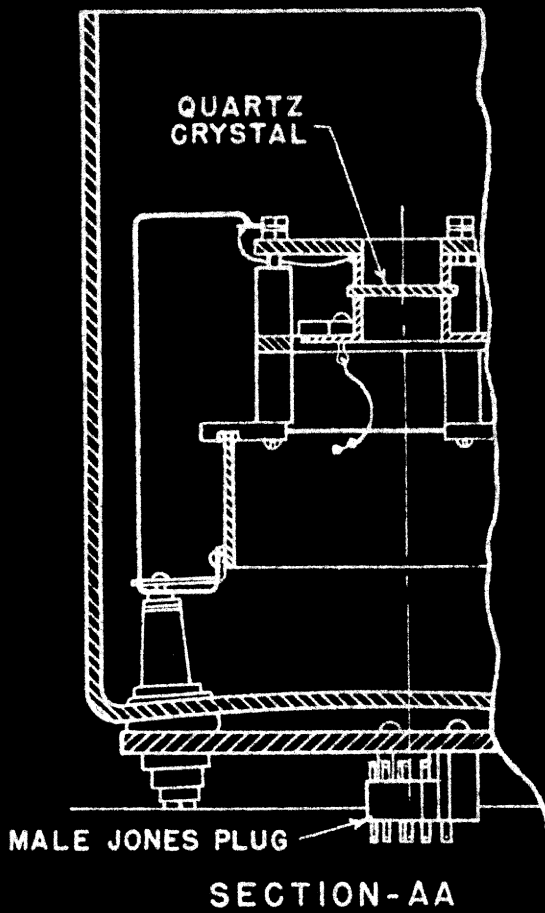
CRYSTAL RESEARCH LABORATORIES
 HAWTHORNE, CALIFORNIA, U.S.A.

Figure 14



Figure 15

Elevation View of Ultrasonicator
From Rear



Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, Virginia

ULTRASONATOR TRANSDUCING CRYSTAL

Scale 3" = 1' - 0"

Drawn By LW-MJB 11-7-47

Checked By DT 11-7-47 Drawing 3

Approved By *R.V.* 12-17-48 Figure 16

Control Of Variables. Emphasis was now placed on fixing the variables involved in so far as practicable. The ultrasonic oscillator used was limited to four frequencies -- namely, 400 kc, 700 kc, 1000 kc, and 1500 kc. Two thousand volts plate voltage may be applied to the quartz crystal plates provided the plate current does not exceed 360 milliamperes. Overloading may result in permanent damage to the equipment.

The impedance matching unit tuning knob was adjusted for each frequency used so that the plate current approached 360 milliamperes when the plate voltage approached 2000 volts. After this adjustment had been made the matching unit tuning knob was maintained in this position for all investigations at the particular frequency and power being used, unless line current fluctuations demanded slight changes of the settings. In order to check for fluctuations the following data (96) may be used as calibration data:

- a. At 1250 volts plate voltage, the plate current should be 210 milliamperes.
- b. At 1740 volts plate voltage, the plate current should be 300 milliamperes.
- c. At 2000 volts plate voltage, the plate current should be 360 milliamperes.

If at the particular plate voltage, the instrument does not show the proper plate current, the matching unit tuning knob should be adjusted to give the proper plate current. At high plate voltages, the milliammeter will fluctuate somewhat due to the normal operating characteristics of the equipment. Consequently, these fluctuations above or below normal should be discounted unless their magnitude is great.

While performing preliminary runs it was found that the energy absorbed by the transducer oil bath gave an undesirable temperature rise in the transformer oil which would prevent runs for extended periods of time or runs for short periods of time when the interval between runs was short. To alleviate this situation, an external cooling unit already described was designed and constructed to maintain the mean oil temperature in the transducer at about 68°F. On trial runs the exit temperature of the oil remained at 55°F to 62°F, depending on the frequency being used and the time of irradiation of the sample.

No attempt was made to control the temperature of the mixture being irradiated other than the cooling caused by the transducer oil bath and control of other factors. Some factors that control the temperature of the mixture being irradiated are:

- a. Period of time irradiated.
- b. Type of container.
- c. Position of container in the transducer oil bath.
- d. Flow of oil through the transducer oil bath container.
- e. Temperature of inlet oil to the oil bath container.
- f. Location of oil inlet and outlet in the transducer.

The flow of oil through the transducer oil bath container was arbitrarily set at one gallon per minute after this was found to give an exit oil temperature of about 60°F and no apparent turbulence in the oil bath container. Also, due to the operating characteristics of the pump being used, much higher rates of oil flow caused an undesirable noise in the pump.

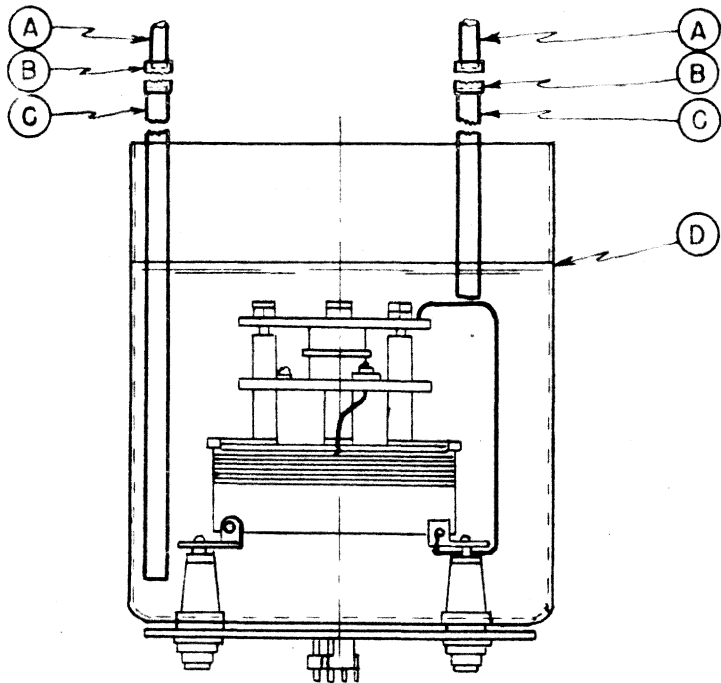
The oil inlet (figure 17) was two centimeters from the bottom of the transducer oil bath container and to the extreme left of the container when looking at the front elevation view.

The oil outlet (figure 17) was one centimeter below the transducer oil bath level and to the extreme rear of the oil bath approximately midway between the transducer coil element and the inside wall of the transducer oil bath container. At all times the level of the oil was maintained three centimeters above the top surface of the coil element porcelain plate of the transducer.

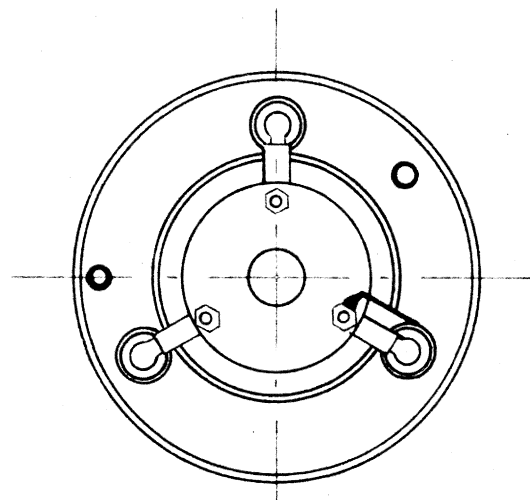
It should be especially noted that the tubes delivering and removing the oil from the bath were glass (7.5 mm ID and 9.5 mm OD). This material of construction was necessary to prevent electrical disturbance of the system and possible damage to the equipment due to an electrical discharge in the oil bath. If some material which easily conducted electricity were used, both of these factors considered could occur.

The oil inlet and oil outlet positions were chosen so that the cooled oil could "push" the warm oil to the top of the oil bath and be removed. In this way the less dense or warm oil was being continually removed and also there was a minimum of mixing of oil in the bath.

The type of container chosen for the mixture to be irradiated was a glass vial shown in figure 18. The selection of the vial was from the standpoint of availability and convenience of handling. However, the attachment shown was necessary to prevent the mixture



ELEVATION



PLAN
AT TOP

LEGEND

- | | |
|-------------------|------------------|
| (A) Copper Tubing | (C) Glass Tubing |
| (B) Tygon Tubing | (D) Oil Level |

REVISIONS

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

OIL INLET AND OUTLET POSITIONS

SCALE 3" = 1'-0"

DRAWN BY WCG 12-7-48

TRACED BY WCG 12-8-48

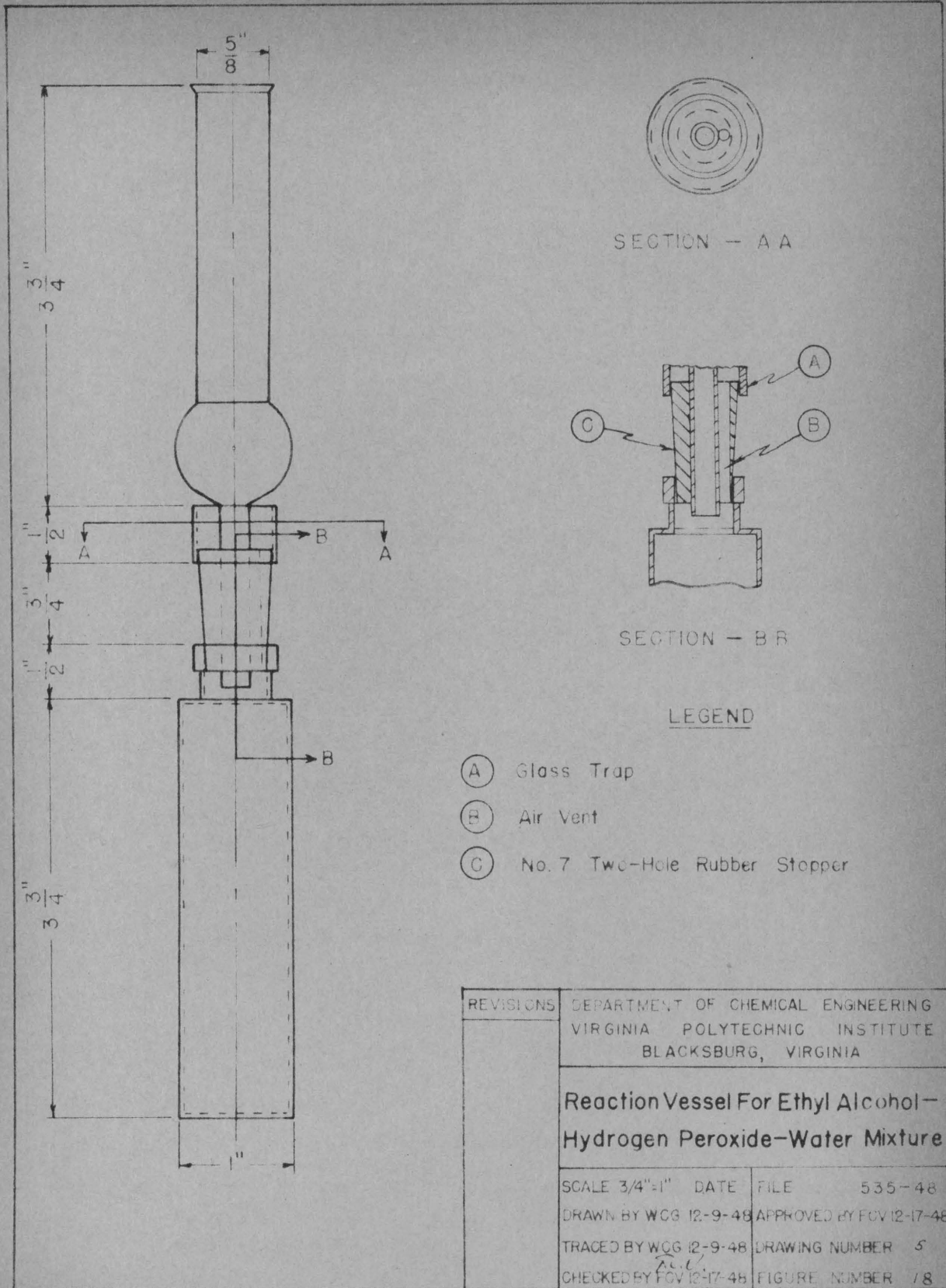
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DRAWING NUMBER 4

FIGURE NUMBER 17



SECTION - A A

SECTION - B B

LEGEND

- (A) Glass Trap
- (B) Air Vent
- (C) No. 7 Two-Hole Rubber Stopper

REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
	Reaction Vessel For Ethyl Alcohol- Hydrogen Peroxide-Water Mixture		
	SCALE 3/4"=1"	DATE	FILE 535-48
	DRAWN BY WCG 12-9-48	APPROVED BY FGV 12-17-48	
	TRACED BY WCG 12-9-48	DRAWING NUMBER	5
	CHECKED BY FGV 12-17-48	FIGURE NUMBER	7/8

being "thrown out" when higher voltages were being applied to the ultrasonicator. Reaction vessels such as erlenmeyer flasks, beakers, round bottomed test tubes, etc were tried using oil and water as the mixture being subjected to ultrasonic irradiation. In these preliminary investigations it was found that the container selected gave the best apparent oil and water emulsion. Weissler and Cooper (201) have pointed out that in certain investigations, a test tube with a very thin glass bottom gave less yield although it transmitted more sound energy than a normal test tube. It is believed that the wall thickness of the tube selected (1.0 - 1.1 mm) for this investigation is a representative mean between the extremes of wall thickness of different containers readily available. The average thickness of the vial bottom was 0.8 mm.

With the aid of the human eye for sighting purposes, the container was clamped as closely as possible in a vertical position (figure 19) with the geometric vertical axis directly over the intersection of the geometric vertical axis and horizontal axis of the quartz crystal plate. The bottom of the container was immersed two centimeters below the transducer oil level or one centimeter above the top surface of the coil element porcelain plate of the transducer.

The period of time of ultrasonic irradiation for a given mixture was arbitrarily set at one minute and twenty minutes respectively for a given power and frequency. This latitude of time was considered sufficient to determine if time of irradiation

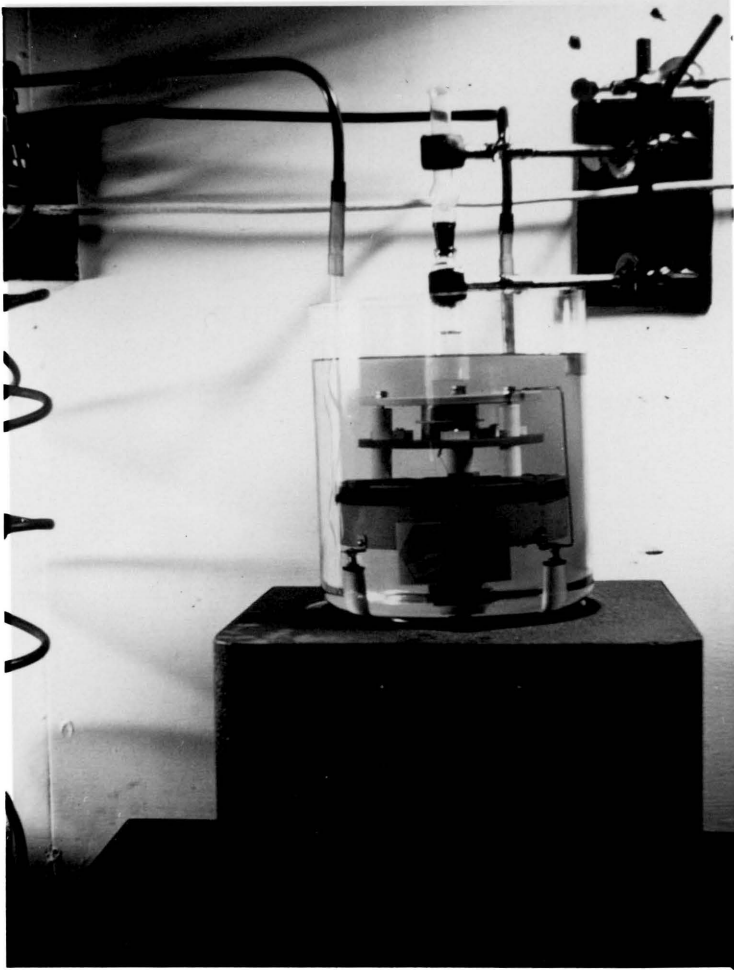
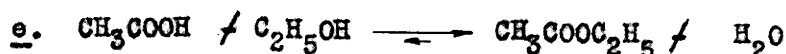
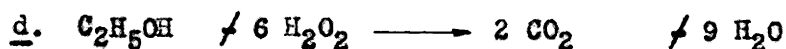
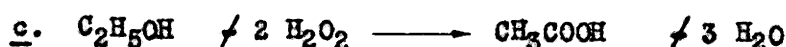
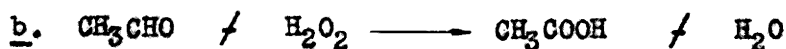
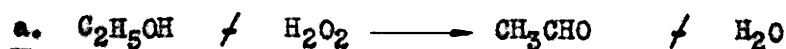


Figure 19

Transducer and Reaction Vessel

has an effect on the mixture. Individual mixtures were irradiated at intervals of 200 volts until the maximum safe plate voltage was reached.

The composition of the mixture to be irradiated depended on the reactions assumed that could take place. These were:



On the basis of the literature review it was believed that:

1. Reaction d is unlikely to occur when using dilute hydrogen peroxide (182).

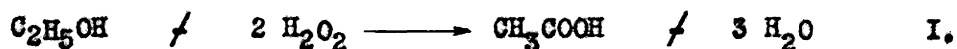
2. Reaction a, b, and c are probable.

3. Reaction e is unlikely, because it is believed ultrasonic irradiation would have a tendency to cause the reverse reaction.

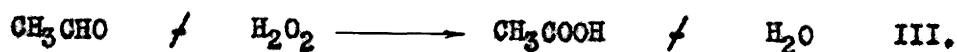
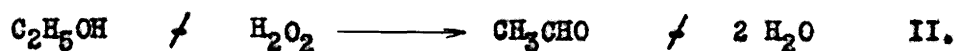
4. The possibility of paraldehyde $(CH_3CHO)_3$ and metaldehyde $(CH_3CHO)_4$ being formed is in all probability slight. In the formation of paraldehyde, a mineral acid such as sulfuric acid is required. The only mineral acid present in the mixture would be that small amount present in hydrogen peroxide. Metaldehyde is unlikely to be formed due to the temperature being employed and the purity of the reagents. Even if minute quantities of these substances were formed, it is possible that the paraldehyde and

metlaldehyde would be depolymerized due to the action of ultra-sonics. It has been shown (2) that paraformaldehyde exhibits a breaking-up action at about 700 kc.

Equation c was assumed for the reaction to take place from the standpoint of the beliefs above and the following thermodynamic considerations: The equation,



may be regarded as composed of the following steps:



Therefore, since all substances which appear in more than one equation are in the same state, the free energy of equation I is equal to the sum of the free energies of equation II and equation III (64).

The simplest way to obtain the free-energy change for equation I was by algebraic combination of the free energies of formation of the various substances concerned. Thus, $\Delta F(\text{reaction}) = \Delta F(\text{formation of } \text{CH}_3\text{COOH}) \not\leftarrow \Delta F(\text{formation of water}) - \Delta F(\text{formation of } \text{C}_2\text{H}_5\text{OH}) - \Delta F(\text{formation of } \text{H}_2\text{O}_2)$ or more simply $\Delta F = \Delta F(\text{products}) - \Delta F(\text{reactants})$.

Lange (50.5) gives the free energy of formation for the substances in equation I at 25°C as follows:

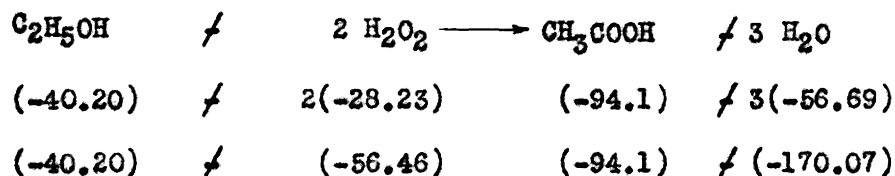
$$\Delta F \quad \text{C}_2\text{H}_5\text{OH} (1) \quad - 40.20 \text{ kg cal}$$

$$\Delta F \quad \text{H}_2\text{O}_2 (1) \quad - 28.23 \text{ kg cal}$$

$$\Delta F \quad \text{CH}_3\text{COOH} (1) \quad - 94.1 \text{ kg cal}$$

$$\Delta F \quad \text{H}_2\text{O} (1) \quad - 56.69 \text{ kg cal}$$

Substituting these values in the equation,



$$\begin{aligned} \text{Then } \Delta F &= \Delta F(\text{products}) - \Delta F(\text{reactants}) \\ &= (-170.07) / (-94.1) - (-40.20) - (-56.46) \\ &= - 167.51 \text{ kg cal} \end{aligned}$$

Since the calculated free energy of this reaction is less than zero, the reaction is promising.

All calculations and methods of analysis chosen were based on the reaction assumed. The composition of the mixture to be irradiated was a given weight of 95 per cent ethyl alcohol plus a given weight of 30 per cent hydrogen peroxide.

A typical calculation for preparing the mixture was as follows:

- a. Alcohol issued for this investigation was 99 per cent by weight. Therefore, 100 gms of 99 per cent alcohol

contains 99 gms of alcohol and 1 gm of water. Each ml of 99 per cent alcohol weighs 0.7893 gms at 20/20°C.

b. If 1 ml of 99 per cent alcohol weighs 0.7893 gms then 0.7893×0.01 (% water) = 0.0079 gms of water in 1 ml. Then $0.7893 - 0.0079 = 0.7814$ gms of alcohol in 1 ml.

c. 121.57 ml of 99 per cent alcohol is required for 95 gms of ethyl alcohol by the relationship:

$$\frac{95 \text{ gms } 100\% \text{ alcohol}}{0.7814 \text{ gms } 100\% \text{ alcohol per ml } 99\% \text{ alcohol.}}$$

Therefore, 121.5 ml of 99 per cent alcohol contains 121.5×0.0079 or 0.959 gms of water.

d. In order to prepare 95 per cent alcohol from 99 per cent alcohol $5.00 - 0.96 = 4.04$ gms of water must be added. The percentage alcohol was checked using a Spencer refractometer and data given by Lange (118) and Hodgman (108) which is shown graphically in figure 20 and figure 21. Dilution using water or the addition of alcohol was made until at least five identical readings were obtained on the refractometer for 95 per cent alcohol.

e. The hydrogen peroxide percentage in the reagent bottle was determined as follows: Ten ml of approximately 30 per cent hydrogen peroxide was diluted to 100 ml with distilled water

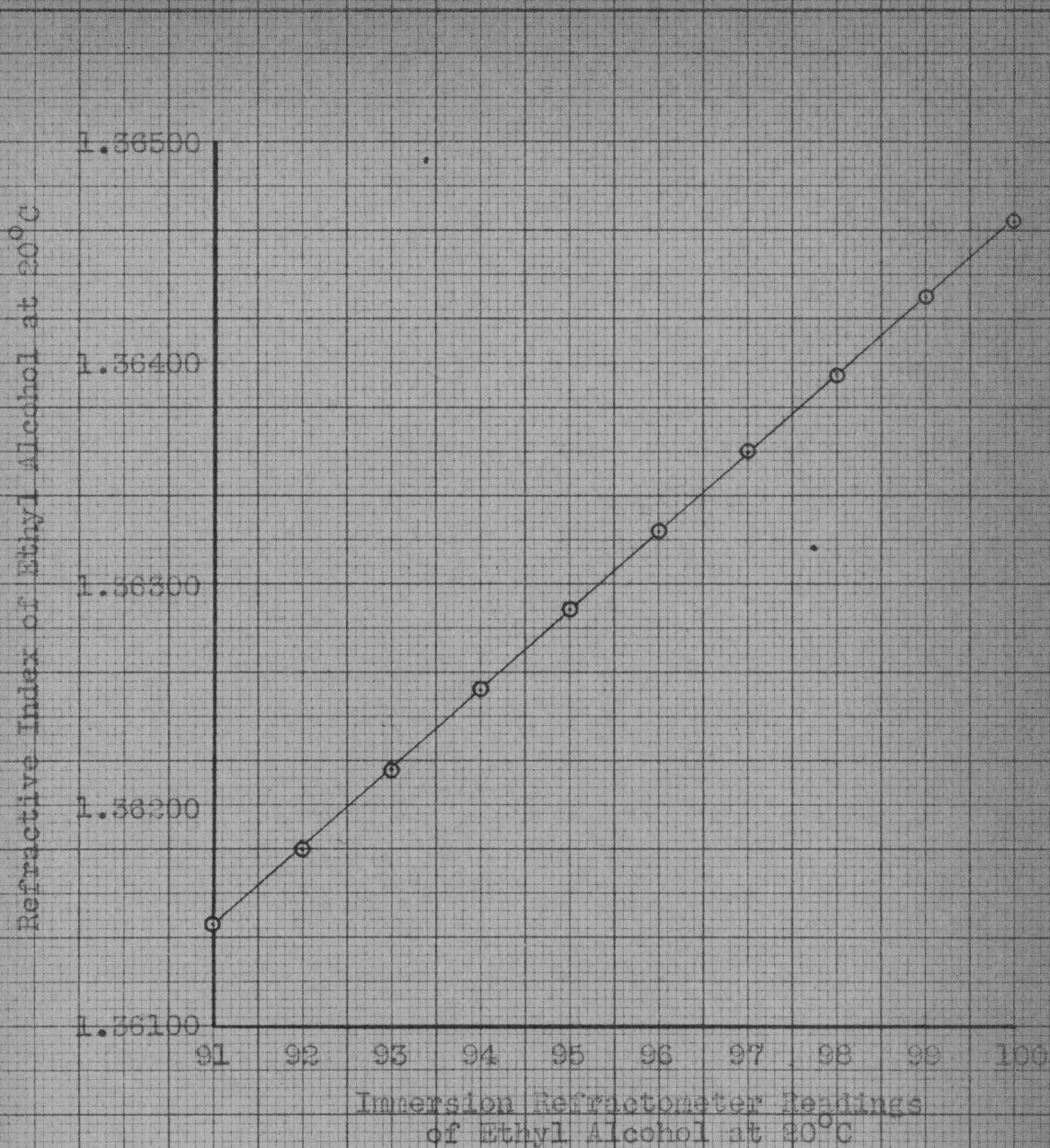


Figure 20

Conversion of Scale Divisions of the Immersion Refractometer to Refractive Index

Lange, H. A. "Handbook of Chemistry." p. 1024. Handbook Publishers, Inc., Sandusky, O. 1946. 6th ed.

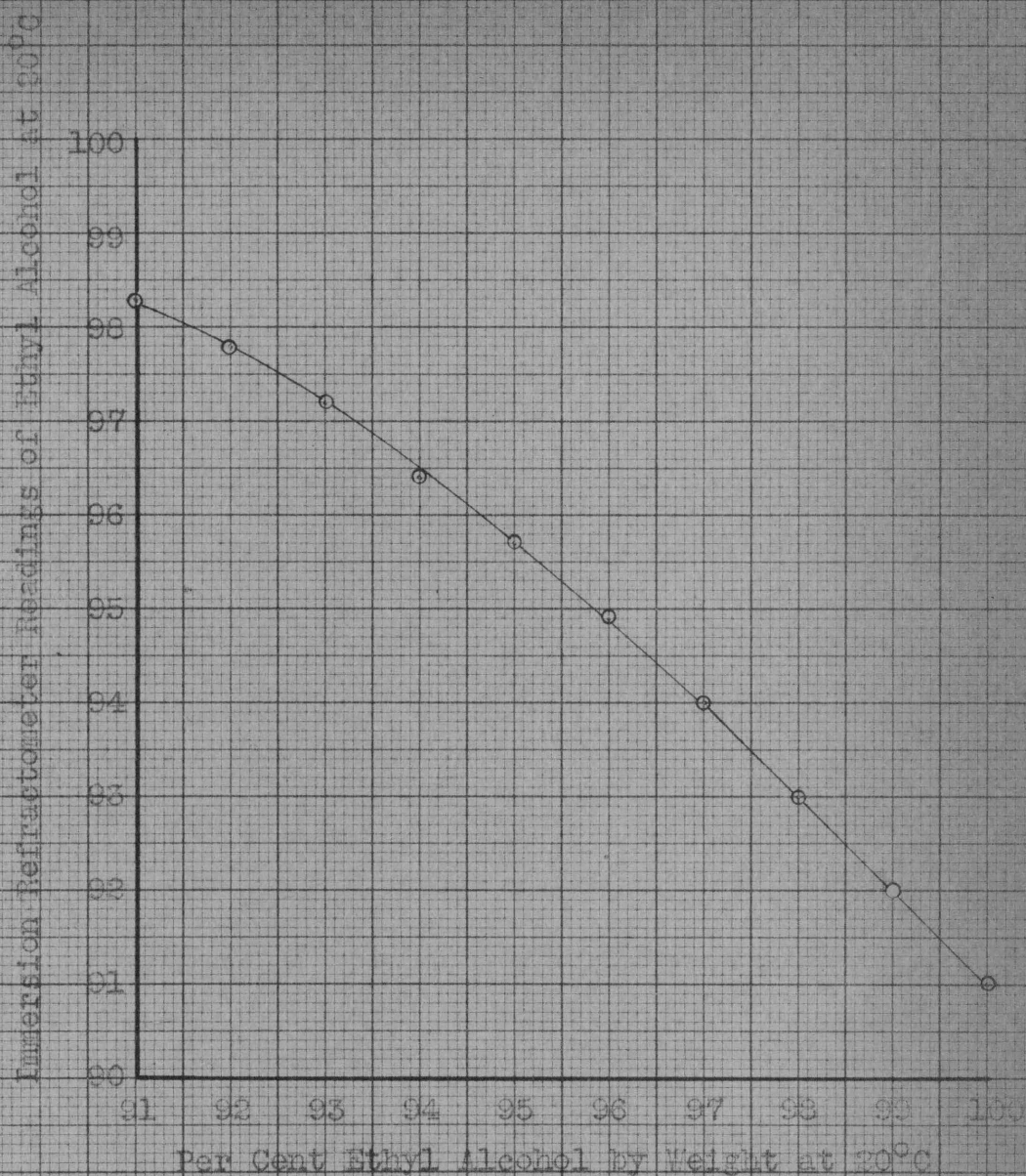


Figure 21

Immersion Refractometer Readings
of Ethyl Alcohol at 20°C.

Hodgman, C. D. "Handbook of Chemistry and Physics."
p. 1632. Chemical Rubber Publishers Co., Cleveland,
O. 1946. 50th ed.

which had been cooled to 20°C. Two ml of the diluted mixture was weighed and titrated with 0.1 N potassium permanganate solution as follows:

wgt of beaker and H ₂ O ₂	52.1174 gms	10.8154 gms
wgt of beaker	50.1225	8.8061
wgt of H ₂ O ₂	<u>1.9949 gms</u>	<u>2.0093 gms</u>
ml 0.1 N K ₂ MnO ₄	39.1 ml	39.4 ml
Hydrogen Peroxide	32.6 %	32.6 %

$$\text{Calculation: ml K}_2\text{MnO}_4 \times N \times 0.017 \times \frac{100}{\text{gm H}_2\text{O}_2} = \% \text{H}_2\text{O}_2$$

f. The specific gravity of the hydrogen peroxide in the reagent bottles was determined as follows:

wgt of pycnometer and water at 20°C	42.6048 gms
wgt of pycnometer	<u>17.6223</u>
wgt of water	24.9825 gms
wgt of pycnometer and H ₂ O ₂ at 20°C	45.4306 gms
wgt of pycnometer	<u>17.6223</u>
wgt of alcohol	27.8083 gms

$$\text{Sp Gr at } 20/20^\circ\text{C is } \frac{27.8083}{24.9825} = 1.1131 \text{ gms per ml}$$

g. Theoretical requirements of hydrogen peroxide assuming the reaction $\text{C}_2\text{H}_5\text{OH} \nearrow 2 \text{H}_2\text{O}_2 \longrightarrow \text{CH}_3\text{COOH} \nearrow \text{H}_2\text{O}$:

Sp gr of 95 per cent ethyl alcohol at 20/20°C is 0.80567. Therefore, $10/46 = x/68$ or 14.78 gms of hydrogen peroxide required for 10 grams of ethyl alcohol on a 100 per cent by weight basis. One ml of 95 per cent by weight alcohol has 0.80567×0.95 or 0.76538 gms of alcohol. Each ml of 32.6 per cent hydrogen peroxide weighs 1.1131 gms at 20/20°C.

Therefore, 1.1131×0.326 or 0.3628 gms of hydrogen peroxide are contained in 1 ml of 32.6 per cent hydrogen peroxide.

Volume of 95 per cent by weight ethyl alcohol required for 10 grams of alcohol is $10/0.76538$ or 13.06 ml of 95 per cent alcohol.

Volume of 32.6 per cent by weight hydrogen peroxide required for 14.78 grams of hydrogen peroxide is $14.78/0.3628$ or 47.38 ml of 32.6 per cent hydrogen peroxide.

The ethyl alcohol-hydrogen peroxide-water mixture used in the investigation was made by mixing 13.06 ml of 95 per cent by weight ethyl alcohol and 47.38 ml of 32.6 per cent by weight hydrogen peroxide.

Considering the analytical procedures to be used, the volume of the mixture to be irradiated was fixed at 15 ml. It is conceded that an excess of 5 ml was irradiated, but due to the use of a pipet in measuring quantities withdrawn from the container, an excess of the mixture was necessary to prevent the mixture being accidentally drawn into the mouth and consequently suffering tissue damage due to the concentration of the hydrogen peroxide being used.

Qualitative And Quantitative Procedures. Emphasis was now directed toward determining analytical procedures which would be rapid and reliable in determining any changes that might be caused in the mixture due to ultrasonic irradiation. Throughout the

investigation all reagents used were as chemically pure as could be ordinarily obtained. All water used in the procedures was double distilled.

As an aid to clarity in understanding the problems encountered and the methods used for analysis, each substance to be sought qualitatively and quantitatively will be discussed separately in the order of hydrogen peroxide, acetaldehyde, pH and "acid" content.

1. Hydrogen Peroxide

Qualitative. The qualitative determination for hydrogen peroxide present in the mixture was discarded because hydrogen peroxide was intentionally present before ultrasonic irradiation. Its presence after ultrasonic irradiation could be detected by the quantitative method for hydrogen peroxide. The reducing substances in the alcohol used in this investigation was not less than 25 minutes permanganate time based on the methods of testing by the U. S. Industrial Chemicals, Inc., Baltimore, Md. Therefore, if potassium permanganate was reduced in the quantitative method for hydrogen peroxide determination, hydrogen peroxide must be present.

Quantitative. The method for quantitative determination is a modification of the methods proposed by Snell and Biffen (186) and Willard and Furman (202). Their method of checking 30 per cent hydrogen peroxide was a simple titration using potassium permanganate. Ten ml of the 30 per cent hydrogen peroxide was diluted to

100 ml with distilled water. A small flask was weighed; 2 ml of the diluted hydrogen peroxide was pipeted into it, and the flask weighed. The sample was rinsed into a 250 ml beaker to which had previously been added 2-3 ml of concentrated sulfuric acid and 75 ml of water. This mixture was then titrated with 0.1 N potassium permanganate to the first pink tinge.

The quantitative method adopted for hydrogen peroxide determination before and after ultrasonic irradiation was: Five ml of the ethyl alcohol-hydrogen peroxide-water mixture which contained hydrogen peroxide was pipeted into a 50 ml glass stoppered volumetric flask. This was diluted with distilled water to the mark; stoppered and shaken. Using a micropipet, 1 ml of the diluted mixture was pipeted into a 150 ml beaker containing 75 ml of sulfuric acid (3 ml of concentrated acid to 75 ml of distilled water). This was titrated with 0.1 N potassium permanganate to the first pink tinge using a microburet. A blank for 75 ml of sulfuric acid should be subtracted from the volume of the potassium permanganate used when making calculations.

2. Acetaldehyde

Qualitative And Quantitative. The literature search revealed the use of Schiff's reagent as the quicker and probably the most sensitive reagent for detecting acetaldehyde. The preparation and method for using this reagent is described in most standard

analytical textbooks. While this method is straightforward from the standpoint of a qualitative test, it was desired to use a method that might possibly be useful for both qualitative and quantitative determinations at the same time.

In this respect the literature search revealed no straightforward and simple approach. Unusual difficulties were experienced in developing a method for acetaldehyde determination. Consequently, this section will be discussed in detail.

Most of the previous investigators used a colorimetric method employing the Schiff's reagent. For preliminary work, the official colorimetric method as given by the Association of Official Agricultural Chemists (121) was used. Hereafter this method will be referred to as the AOAC method. This method was:

"16.14

REAGENTS

(a) Aldehyde-free alcohol. -- Redistil alcohol over NaOH or KOH, add 2-3 g per liter of metaphenylenediamine hydrochloride, digest at ordinary temp. several days (or under reflux condenser on steam bath several hours), and distil slowly, rejecting first 100 ml and last 200 ml of distillate.

(b) Sulfite-fuchsin soln. -- Dissolve 0.50 g of pure fuchsin in 500 ml of H₂O, add 5 g of SO₂ dissolved in H₂O, make up to 1 liter, and allow to stand until colorless. As this soln decomposes rapidly, prepare it in small quantities and keep at low temp.

(c) Standard acetaldehyde soln. -- Prepare as follows (1):

Grind aldehyde ammonia in mortar with anhydrous ether and decant the ether. Repeat this operation several times and dry purified salt in current of air and then in vacuo over H_2SO_4 . Dissolve 1.386 g of this purified aldehyde ammonia in 50 ml of alcohol, add 22.7 ml of N alcoholic H_2SO_4 , make up to 100 ml with alcohol, and add 0.8 ml of alcohol for the volume of the $(NH_4)_2SO_4$ precipitate. Allow mixture to stand overnight, and filter. This soln contains 1 g of acetaldehyde in 100 ml and will retain its strength.

Dilute 2 ml of above soln to 100 ml with alcohol (50% by volume). 1 ml = 0.0002 g of acetaldehyde. Prepare soln every day or so.

16.15

DETERMINATION

..... Dilute 5-10 ml of distillate to 50 ml with aldehyde-free alcohol, 50% by volume; add 25 ml of the sulfite-fuchsin soln, and allow to stand 15 min. at 15° . Solns and reagents should be at 15° when they are mixed. Prepare standards of known strength and blanks in same way....."

Reagents were prepared as described above using the following materials:

Ethyl Alcohol. USP, 190 proof, serial number 171457,

U. S. Industrial Chemicals, Inc., Baltimore, Md.

Fuchsin, Basic. Total dye content 91%. Certification number NF 54. National Aniline Division, Allied Chemical and Dye Corporation, New York.

Sulfur Dioxide solution was prepared by bubbling sulfur dioxide gas through distilled water until the weight of the solution had increased five grams.

Aldehyde Ammonia. CP, crystal, Lot number 472365, Eimer and Amend, New York.

Sulfuric Acid. CP, Sp gr at 60°F Min 1.84. Eimer and Amend, New York.

Diethyl Ether. CP, anhydrous. Lot number 477353. Eimer and Amend, New York.

In order to observe this colorimetric method a mixture consisting of 6 ml of ethyl alcohol (190 proof) and 20 ml of approximately 30 per cent hydrogen peroxide was prepared. To 10 ml of this mixture enough 50 per cent by volume methyl alcohol (Synthetic Absolute, Code 1214, Lot number C 205 J, General Chemical Co., New York) was added to make 50 ml. Synthetic methyl alcohol was substituted for ethyl alcohol because it is supposed to be consistently aldehyde free; cost is less; and Biffen and Snell ⁽²⁸⁾ state it has been used largely to replace the ethyl alcohol in this determination for several years. One ml of standard acetaldehyde solution was added to this mixture and then 25 ml of fuchsin-sulfite solution. Immediately a faint pink color was observed on gently mixing.

A 50 ml nessler tube was filled to the mark with this mixture and placed in a water bath at 15°C for 15 minutes. The remaining portion of this mixture was poured into a 50 ml nessler tube and placed in a nessler tube rack at room temperature (28°C).

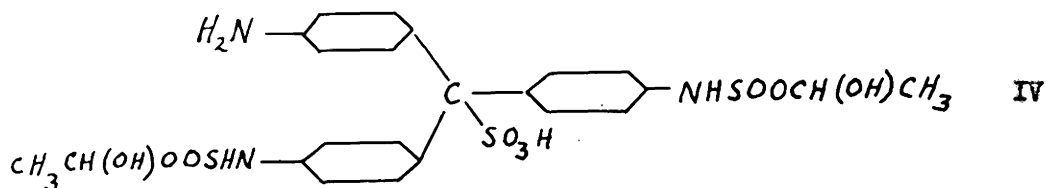
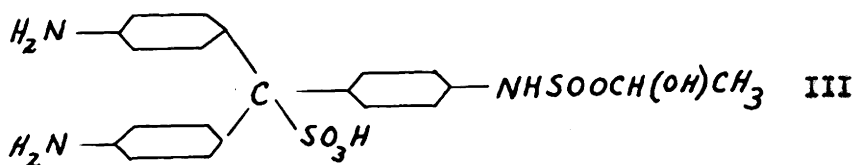
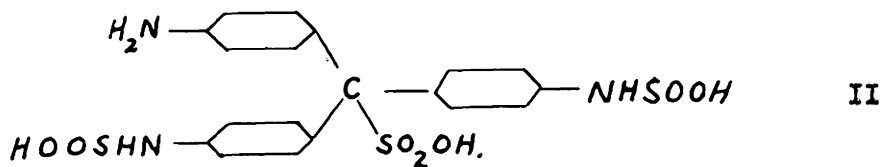
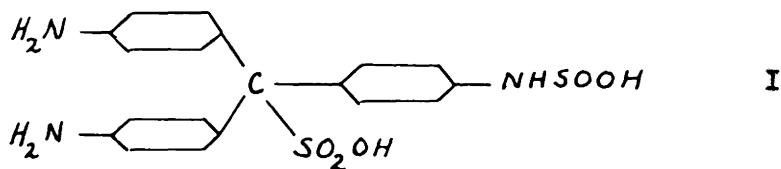
The same procedure was immediately repeated using 50 ml of 50 per cent by volume ethyl alcohol, 1 ml of standard acetaldehyde solution, and 25 ml of fuchsin-sulfite solution. A brilliant magenta color was observed on gently mixing. Nessler tubes were filled and treated in the same manner as with the 10 ml ethyl alcohol-hydrogen peroxide-water mixture.

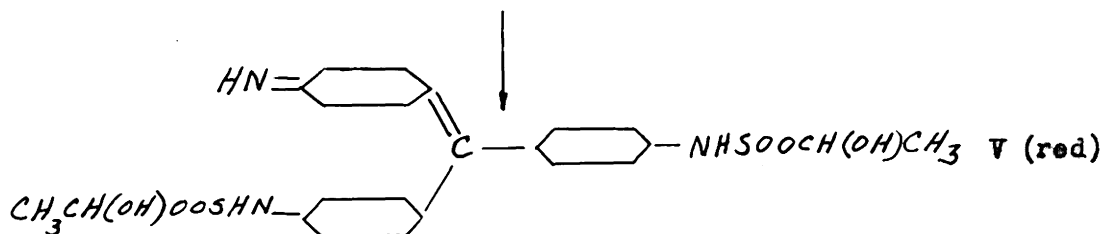
At the end of 15 minutes the color in the nessler tube containing the ethyl alcohol-hydrogen peroxide-water mixture at 15°C appeared less intense than at zero time. That portion in the nessler tube at 28°C showed apparently the same coloration or was a little darker than the coloration at zero time; this was difficult to determine by eye. No explanation was advanced for this phenomenon.

At the end of 15 minutes the color in the nessler tube at 15°C and containing only ethyl alcohol showed an increase in intensity while the color in the tube at 28°C showed an even darker color.

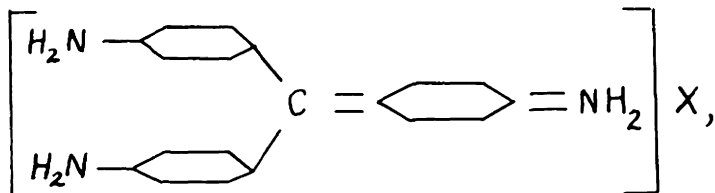
All four nessler tubes were placed in a nessler tube rack at room temperature (28°C) for six hours. It was noted that the tube containing the ethyl alcohol and hydrogen peroxide at 15°C gained color intensity and appeared to have the same intensity as the tube kept at 28°C which seemed to retain its color intensity. The color in

the nessler tubes not containing hydrogen peroxide faded considerably until only a pink color was observed in both tubes. According to Karrer (112) this loss of color is due to the following reactions:





Karrer states that the red dye, parafuchsine,



is converted by sulfur dioxide into a colorless compound, which contains the N-sulphinic acid of parafuchsine-leuco-sulphonic acid (I or II).

On addition of aldehyde the colorless compounds III and IV are formed. The latter loses the sulphonic group attached to the carbon atom, and gives the red (quinonoid) dye, V. After some time, compound V decomposes into acetaldehyde-bisulphite and fuchsin-sulphurous acid, and decolorization of the liquid again occurs.

It was decided to repeat these preliminary investigations and omit the standard acetaldehyde solution. The same results were observed except the color intensity was less, due to the absence of the standard acetaldehyde solution. This showed that the methyl alcohol gave a positive test for aldehydes and must therefore be purified or discarded.

Ethyl alcohol (190 proof) was substituted for the methyl alcohol and the same procedure repeated without standard acetaldehyde solution or hydrogen peroxide. Again a comparatively intense

magenta color developed. Therefore, the only resort to obtain aldehyde-free alcohol from that on hand for this investigation and this particular colorimetric method is by purification.

For the purification of the ethyl alcohol (190 proof), 1500 ml was poured into a 2 liter round bottom pyrex glass flask. This was immersed and clamped in a vertical position in a pneumatic trough water bath supported by a tripod. Twenty five grams of sodium hydroxide (CP pellets, Lot number 102645. J. T. Baker Chemical Co., Phillipsburg, N. J.) was added to the ethyl alcohol. A two-hole number 10 rubber stopper fitted with a glass safety tube and a glass delivery tube (7.5 mm ID) was fitted to the neck of the 2 liter flask. A two foot glass liebig condenser with a 16 inch cooling jacket was connected to the delivery tube using a number 10 cork.

A small 110 volt AC electric laboratory type stirrer and a glass thermometer (0-100°C) were clamped to a ringstand and placed adjacent to the water bath in such a manner that the stirrer rotor and the bulb of the thermometer were immersed in the water bath. Heat was applied to the water bath by illuminating gas using a Fisher burner. While heat was being applied the electric stirrer was in operation to keep the temperature of the bath at approximately 90°C.

The ethyl alcohol was distilled off until about 100 ml remained in the flask which was discarded. The distillate was returned to the cleaned 2 liter flask and 2.5 grams of metaphenylenediamine hydrochloride (CP, Lot number 474552. Eimer and Amend, New York) was

added. The condenser was placed in a vertical position to serve as a reflux condenser. Heat was applied to the water bath by the Fisher burner and the alcohol-hydrochloride mixture was refluxed for four hours at approximately 90°C.

After refluxing the mixture, glass beads were added to the flask, and the condenser attached in a position for distilling off the ethyl alcohol. Heat was applied and the water bath kept at about 90°C. The first 10 ml of the distillate was checked for aldehydes using the AOAC method. A positive test was observed with a comparatively intense magenta color. Distillation was continued. When approximately 100 ml of the distillate had been collected the rubber stopper in the neck of the 2 liter flask suddenly blew out and was followed by some of the mixture in the flask. The alcoholic mixture fell to the outside of the pneumatic trough and caught fire from the burning illuminating gas used for heating the water bath. In turn the flame advanced into the 2 liter flask and the whole mass ignited which sent the remaining portion of the alcoholic mixture into the room partially covering the walls, ceiling, table, equipment, etc. No explanation can be given for this reaction.

The purification method just described was repeated in the same manner except a porcelain water bath was substituted for the pneumatic trough and steam was used as a supply of heat to eliminate the open flame previously used. Glass beads and small chips of glass tubing were kept in the distilling flask at all times.

When distillation was being made after refluxing with the metaphenylenediamine hydrochloride, the first 100 ml came over at an even rate. Shortly after this, the whole mass seemed to be in a state of ebullition which forced some of the mixture out of the safety tube to a height of about three feet. Also a portion was forced into the condensing tube of the liebig condenser.

This phenomenon could be repeated at will about every 30 seconds by jarring the table on which the equipment rested or by jarring almost any part of the equipment -- especially the distilling flask. With one exception, no further work on the purification of alcohol using metaphenylenediamine hydrochloride was carried out because of this phenomenon.

No explanation can be given for this ebullition but it is interesting at this point to note some of the controversies in the literature concerning this method of purification. Woodman and Lyford (210) observed that metaphenylenediamine hydrochloride seems to remove comparatively slight amounts of aldehyde so that it is essential that the alcohol be relatively pure before being treated with this reagent. It was suggested that some preliminary reagent be used which will remove the greater portion of the aldehyde.

Dunlap (66), Woodman and Lyford (210) secured better results in far less time in this preliminary removal by using silver oxide instead of the caustic potash treatment. Woodman and Lyford also found that the greater portion of the metaphenylenediamine

hydrochloride takes no part in the reaction and good results in aldehyde removal were unsuccessful when using a less proportion than 25 grams to the liter. They theorize that if 3 to 5 grams of fresh metaphenylenediamine hydrochloride were added occasionally, 5 or 6 liters of purified alcohol might be obtained from 30 to 35 grams of the reagent. In this respect the method of the AOAC and other authors certainly disagree.

From the slight solubility of the metaphenylenediamine hydrochloride in alcohol, together with the very large excess that is necessary to use, it seemed probable to Woodman and Lyford that the reaction was very largely a question of the actual surface of the reagent brought into contact with the alcohol. Such being the case, it seemed probable that the only purpose served by boiling for several hours as recommended is to keep the mixture of alcohol and reagent constantly stirred.

Work by Woodman and Lyford confirmed this theory and found that the same results could be obtained by shaking the reagent and the alcohol in a shaking machine at room temperature, as by boiling for the same length of time. They also found that by allowing the reagent and the alcohol to stand for several weeks with frequent shaking proved sufficient to give a fairly good grade of alcohol. Their best results, however, were obtained by keeping the mixture stirred up for several hours by simply drawing a rather vigorous current of air through it.

At this point there was much speculation on methods to remove the aldehyde content of the 190 proof ethyl alcohol. Three possible methods were decided upon. These were:

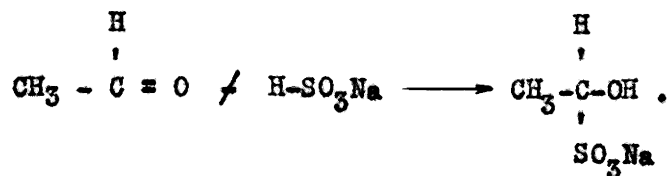
1. Add an excess of solid sodium hydroxide to the ethyl alcohol, dissolve by shaking, and distill.
2. Add an excess of solid sodium hydroxide to the ethyl alcohol, dissolve by shaking and let stand for a week with occasional shaking. Then distill off the alcohol.
3. Repeat 2 above and redistill the distillate and collect in 50 ml fractions. Examine each fraction for aldehyde content by the AOAC method.

No positive results were obtained in any of these methods except the aldehyde content of method 3 seemed to lessen on each 50 ml fraction collected. In using these methods it was observed that a heavy dark brown "gunk" was formed when the sodium hydroxide had been present with the alcohol about 24 hours. With the addition of heat this effect occurred more quickly. According to Hill and Kelley (107) acetaldehyde heated with a concentrated solution of sodium hydroxide produces a yellow, oily, resinous material, the color of which changes to orange and then to red-brown upon continued heating; the product has a characteristic, sweet, sickening odor called "aldehyde resin" which is probably formed by the irreversible polymerization of acetaldehyde, accompanied by the loss of water, so that substances with fairly long, conjugated carbon chains result.

Two other methods were now tried. These were:

1. Two and one-half grams of metaphenylenediamine hydrochloride was added to the distillate of method 2 just discussed.

2. The 50 ml fractions of method 3 just discussed were poured into one container and 2.4 grams of sodium bisulfite (CP granular. Lot number 122347. J. T. Baker Chemical Co., Phillipsburg, N. J.) was added. This amount was calculated on the basis that in 800 ml of alcohol there would be 1 gram of aldehydes. The reaction should proceed according to the equation,



After setting for three days with occasional shaking, the supernatant liquid was decanted off and distilled.

No positive results were obtained in either of these methods. In the first method the violent state of ebullition described previously occurred. This tends to point out that the metaphenylenediamine hydrochloride has some effect in causing this phenomenon. In the second method a thick, white, flocculent mass was formed about 12 hours after the sodium bisulfite had been added. This gradually settled to the bottom of the container which permitted the supernatant liquid to be drawn off for the subsequent distillation.

Work on the purification of the 190-proof ethyl alcohol was stopped and the U. S. Industrial Chemical Co., Baltimore, Maryland,

consulted about this particular lot of alcohol. This company only made reference to page 15 of their technical bulletin entitled "U.S.I. Industrial Alcohol," copyright 1948, in regards to the alcohol. This bulletin states that ethyl alcohol, USP, 190 proof, has the following specifications:

"Acidity: Free acid as acetic acid, not more than 0.0014 gm per 100 cc.

Color: Water-white.

Non-volatile Matter: Not more than 0.0025 gm per 100 cc.

Odor: Free from foreign odors when tested at high or low proof.

Purity: Not less than 95% ethyl alcohol by volume.

Reducing substances: Not less than 45 minutes permanganate time.

Specific Gravity: At 60°/ 60°F - not more than 0.8158."

As a last resort to obtain "pure" alcohol, five gallons of ethyl alcohol, absolute, USP, 200 proof, was ordered from U. S. Industrial Chemicals, Inc., Baltimore, Maryland, which had the following specifications:

"Acidity: Free acid as acetic, not more than 0.0014 gm per 100 cc.

Color: Water-white.

Non-volatile Matter: Not more than 0.0025 gm per 100 cc.

Odor: Free from foreign odors when tested at high or low proof.

Purity: Not less than 99.9% ethyl alcohol by volume.

Reducing substances: Not less than 25 minutes permanganate time.

Specific Gravity: At 60°/60°F - not more than 0.794."

On receiving this alcohol (Serial number 176703), extreme care was exercised in removing a sample to be tested for aldehydes using the AOAC method. Disappointingly enough, a positive test was observed with this alcohol and also with some "absolute" alcohol prepared by the VPI Chemistry Department.

Since aldehyde free ethyl alcohol could not be purchased nor prepared in the laboratory, the idea of purifying the alcohol was abandoned. However, before abandonment it was desired to investigate the fuchsin-sulfite solution itself. According to the AOAC method used, the fuchsin-sulfite solution should be colorless. That solution prepared by the investigator had a decided yellowish-orange tint and on standing would not become colorless.

Two other lots of basic fuchsin were used in preparing fresh solutions. These were:

a. Fuchsin, Basic. Total dye content 77 per cent.

Certification Number NF 23. National Aniline & Chemical Co., Inc., New York.

b. Fuchsin, Basic. Lot number 370724. The Coleman & Bell

Co., Norwood, O.

The fuchsin-sulfite solution prepared using the National Aniline & Company product gave a darker (brownish-yellow) coloration than the

fuchsin used originally. That manufactured by the Coleman & Bell Company gave a colorless solution and was used for the remainder of the investigation.

Some method now had to be sought whereby the aldehyde content originally present in the ethyl alcohol could be estimated in order that the effects of ultrasonic irradiation could be ascertained. Resort was made to the use of a Klett-Summerson Photoelectric Colorimeter. In using this instrument it was desired to find out if a calibration curve could be made. It was planned to use known quantities of standard acetaldehyde solution in the ethyl alcohol-hydrogen peroxide-water mixture and then use the fuchsin-sulfite solution for color formation.

The reasoning behind this possibility is as follows: Assume the colorimeter has been prepared for a test. If the prepared ethyl alcohol-hydrogen peroxide-water mixture is used as a blank and the potentiometer indicator of the colorimeter set on zero, this point may be plotted as 0,0 on the graph shown in figure 22. Now prepare a mixture of the ethyl alcohol-hydrogen peroxide-water-fuchsin-sulfite solution. Allow it to stand 15 minutes at 15°C. Substitute, without changing the zero setting of the colorimeter, this colored solution for the ethyl alcohol-hydrogen peroxide-water mixture used for point 0,0. A potentiometer reading above zero will result due to the magenta color produced. This reading will be a blank for the ethyl alcohol-hydrogen peroxide-water mixture without acetaldehyde being

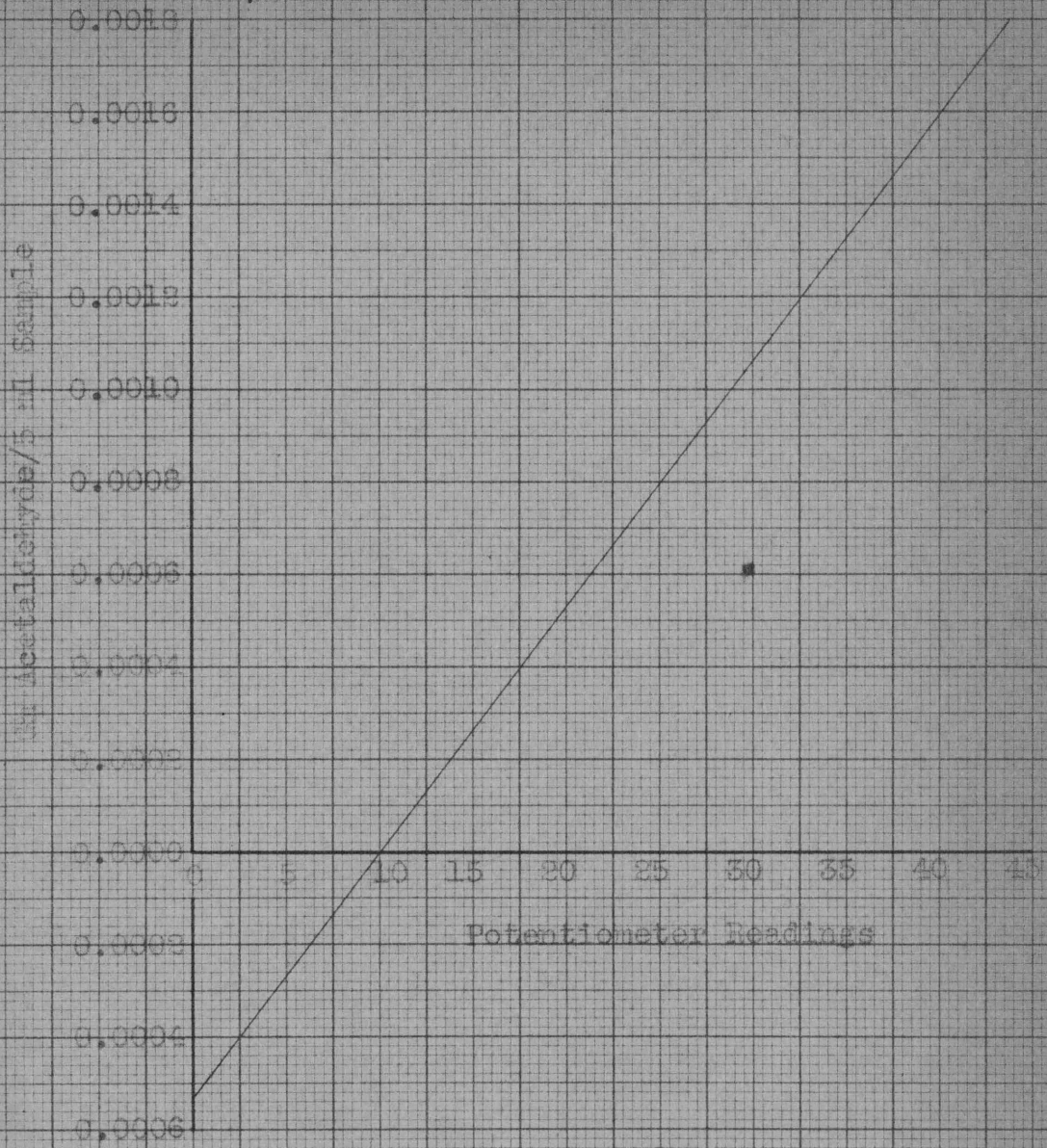


Figure 32

Theoretical Curve for Conversion of Potentiometer Readings on Klett-Summerson Photoelectric Colorimeter to Grams of Acetaldehyde

added. Therefore, this potentiometer reading may be assumed as the reading where no aldehyde is present.

If this procedure is repeated over and over, except adding increasingly known quantities of standard acetaldehyde solution, the magenta color produced should increase in intensity and give higher potentiometer readings. This data may give a straight line relationship and in such a case the apparent aldehyde content in the original mixture could be estimated by inverting the ordinate scale and extrapolating below zero. By using this prepared curve the relative effect on the mixture by ultrasonic irradiation could be determined in so far as the aldehyde content is concerned.

All previous investigators using the fuchsin-sulfite colorimetric test specify that the temperature of the sample being examined and the reagents being used should be at 15°C. Yoe ⁽²¹²⁾ states that the temperature of the room should not be much above 15°C. In this respect, Yoe's suggestion cannot be concurred in because his method specified that the sample and reagents be kept at 15°C when mixed and then kept at 15°C in a water bath for 15 minutes. If the cooled sample is immediately placed in a color comparator and compared with standards there is no necessity for keeping the room temperature at 15°C.

Yoe further states that "the intensity of color developed by acetaldehyde under" the conditions stated "is not in direct proportion to the amount of aldehyde present." Tolman ⁽¹⁹⁷⁾

observed that "a standard containing 0.001 gram" of acetaldehyde "develops about three times as much color as a standard" containing "0.0005 gram and about one-half the color of a standard containing 0.0015 gram."

At this point the strict statements of Yoe and Tolman were doubted when hydrogen peroxide was present in the mixture. During preliminary work using ethyl alcohol-hydrogen peroxide-water mixtures, it was observed that at 15°C the coloration produced using the AOAC method was much less than the coloration produced at the same temperature when only ethyl alcohol and water were used. Another observation was that the intensity of the ethyl alcohol-water-fuchsin-sulfite mixture lessened after a period of time while that of the ethyl alcohol-hydrogen peroxide-water-fuchsin-sulfite mixture appeared to deepen or remain the same. The only obvious conclusion was that the hydrogen peroxide affected the reaction in some way.

It was desired to check the validity of the proposed method using the colorimeter and also devise a method to reduce the quantities of reagents used for the test on the basis of economy. It was decided to use one-fifth the requirements of the AOAC method, except reduce the volume of 50 per cent ethyl alcohol required by the volume of standard acetaldehyde solution added. This reduction of the 50 per cent ethyl alcohol was necessary because the standard acetaldehyde solution was also made up with 50 per cent alcohol. The data obtained for this method are shown in Table I.

TABLE I

Experimental Data For The Development Of A Colorimetric Quantitative Method For Acetaldehyde Determination At 15°C In An Ethyl Alcohol-Hydrogen Peroxide-Water Mixture Using One-Fifth The Volume Requirements Of Reagents For The AOAC Colorimetric Method Corrected For The Volume Of 50 Per Cent Ethyl Alcohol In The Standard Acetaldehyde Solution,

Ethyl Alcohol-Hydrogen Peroxide-Water Mixture	Standard Acetaldehyde Solution	50 Per Cent Ethyl Alcohol	Fuchsin-Sulfite Solution	Potentiometer Scale Reading
	1 ml = 0.0002 gm Acetaldehyde			

ml	ml	ml	ml	
5	0	10	5	18
5	1	9	5	23
5	2	8	5	28
5	3	7	5	33
5	4	6	5	38
5	10	0	5	57

It was found that distilled water gave the same zero reading on the colorimeter as an ethyl alcohol-hydrogen peroxide-water mixture. Therefore, for all zero settings of the Klett-Summerson Photoelectric Colorimeter, distilled water was substituted for the ethyl alcohol-hydrogen peroxide-water mixture. On the whole very little was gained from this experiment as a blank for more than 0.0020 gms of acetaldehyde could not be made. The standard acetaldehyde solution also had a slight brownish color and prevented a true potentiometer reading in such small volumes. Figure 23 is a plot of the data shown in Table I. Examination of the curve showed a confirmation of the proposed method of procedure on the basis of a single trial which certainly was not considered conclusive.

Resort was now made to the volumes recommended by the AOAC method and the above experiment repeated at 15°C with correction for the 50 per cent ethyl alcohol in the standard acetaldehyde solution being made after 10 ml were added. The data of this experiment are shown in Table II. Figure 24 shows a plot of these data which also tend to confirm the proposed method of procedure. In this experiment, the dilution volumes were not kept exactly equal and also a few points seemed to be erratic. Therefore, this experiment was repeated holding the dilution volume constant by correcting for the volume of 50 per cent ethyl alcohol in the standard acetaldehyde solution. The data of this experiment are shown in Table III and a plot of these data is shown in figure 25.

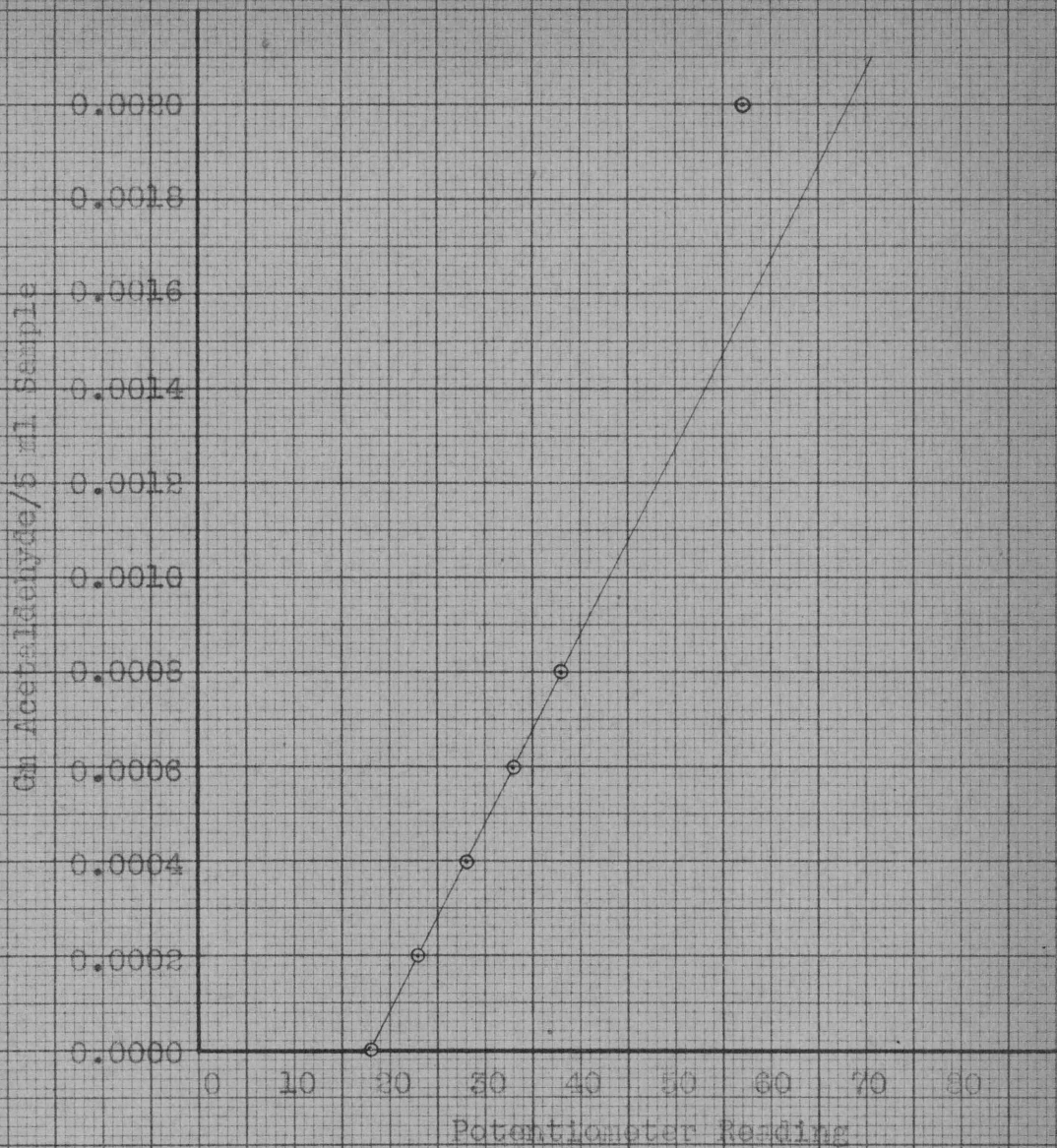


Figure 23

Results of Determination of Acetaldehyde at 15°C Using Klett-Summerson Photoelectric Colorimeter on an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture and One-Fifth the Volume Requirements of Reagents for the AOAC Colorimetric Method Corrected for the Volume of 50 Per Cent Ethyl Alcohol in the Standard Acetaldehyde Solution.

TABLE II

Experimental Data For The Development Of A Colorimetric Quantitative Method For Acetaldehyde Determination At 15°C In An Ethyl Alcohol-Hydrogen Peroxide-Water Mixture Using The Volume Requirements Of Reagents For The AOAC Colorimetric Method Corrected For The Volume Of 50 Per Cent Ethyl Alcohol In The Standard Acetaldehyde Solution After 10 Milliliters Of The Standard Acetaldehyde Solution Was Added.

Ethyl Alcohol-Hydrogen Peroxide-Water Mixture	Standard Acetaldehyde Solution 1 ml = 0.0002 gm Acetaldehyde	50 Per Cent Ethyl Alcohol	Fuchsin-Sulfite Solution	Potentiometer Scale Reading
ml	ml	ml	ml	
5	0	50	25	25
5	1	50	25	26
5	2	50	25	27
5	3	50	25	30
5	6	50	25	35
5	9	50	25	40
5	18	32	25	55
5	25	25	25	66

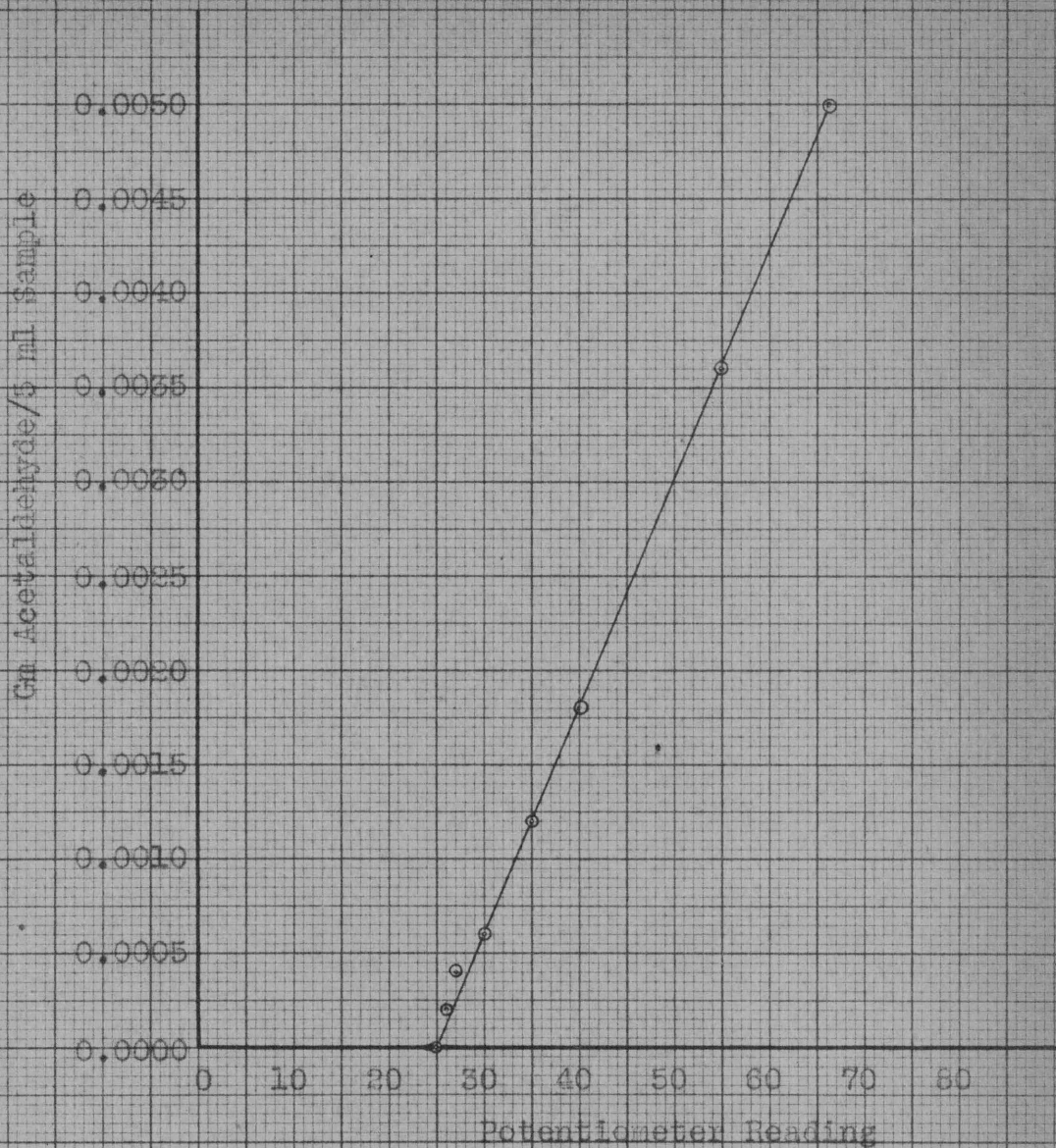


Figure 24

Results of Determination of Acetaldehyde at 15°C Using Klett-Summerson Photoelectric Colorimeter on an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture and the Volume Requirements for the AOAC Colorimetric Method Corrected for the Volume of 50 Per Cent Ethyl Alcohol in the Standard Acetaldehyde Solution after 10 Milliliters of Standard Acetaldehyde Solution was Added.

TABLE III

Experimental Data For The Development Of A Colorimetric Quantitative Method For Acetaldehyde Determination At 15°C In An Ethyl Alcohol-Hydrogen Peroxide-Water Mixture Using The Volume Requirements Of Reagents For The AOAC Colorimetric Method Corrected For The Volume Of 50 Per Cent Ethyl Alcohol In The Standard Acetaldehyde Solution.

Ethyl Alcohol-Hydrogen Peroxide-Water Mixture	Standard Acetaldehyde Solution	50 Per Cent Ethyl Alcohol	Fuchsin-Sulfite Solution	Potentiometer Scale Reading
ml	1 ml = 0.0002 gm Acetaldehyde	ml	ml	
5	0	50	25	35
5	2	48	25	37
5	4	46	25	39
5	6	44	25	39
5	10	40	25	35

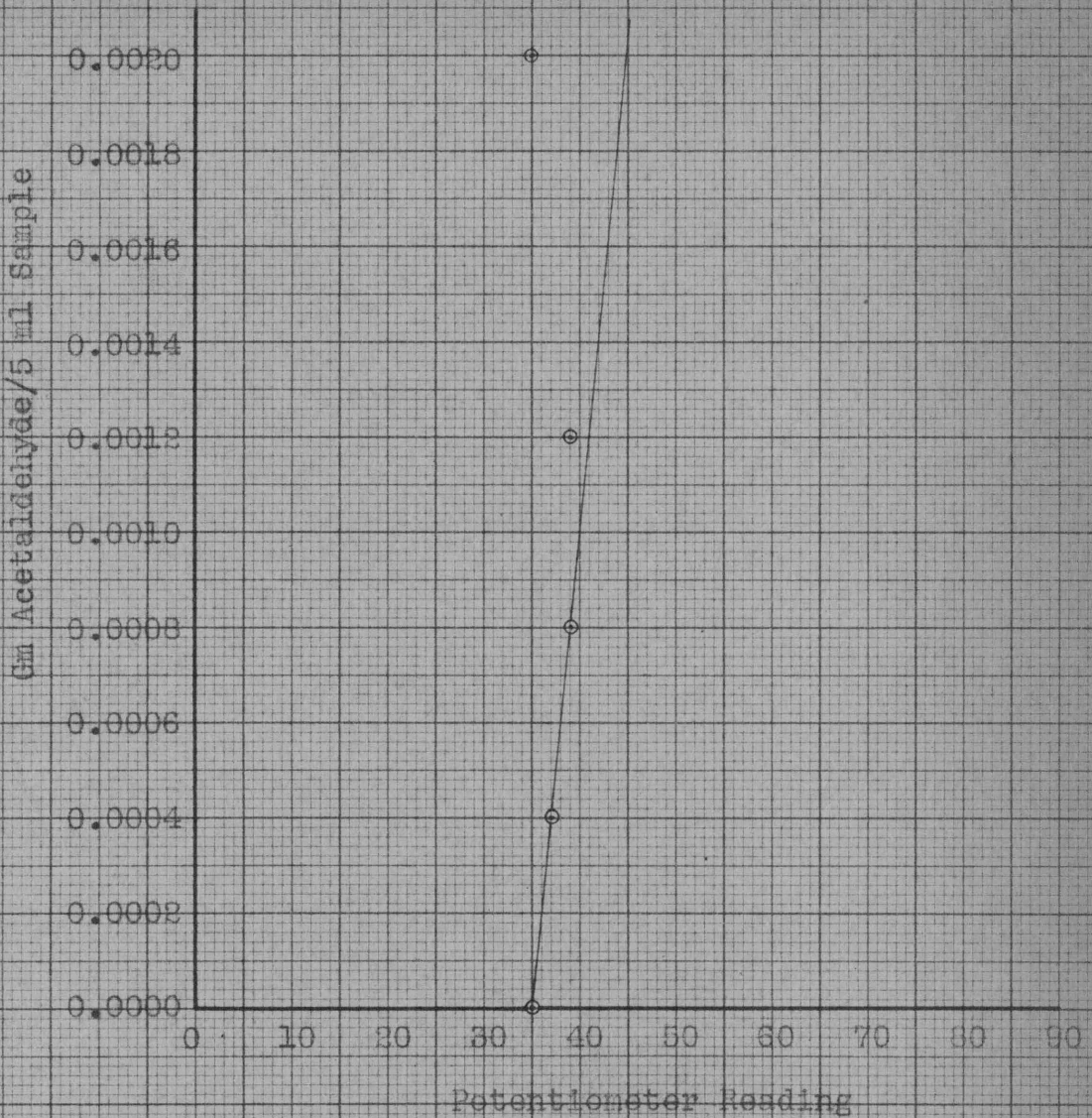


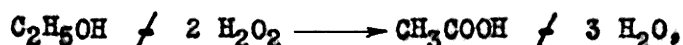
Figure 35

Results of Determination of Acetaldehyde at 15°C Using Klett-Summerson Photoelectric Colorimeter on an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture and the Volume Requirements for the AOAC Colorimetric Method Corrected for the Volume of 50 Per Cent Ethyl Alcohol in the Standard Acetaldehyde Solution.

Examination of the data in Table III showed that at the greatest acetaldehyde content, the potentiometer reading was the same as for the blank. It was found on checking the colorimeter that it did not give a zero reading for the blank. This deviation was due to line current fluctuations. Therefore, it was necessary that the zero setting of the blank be checked just prior to any one determination.

It was almost impossible to duplicate the preparation of the fuchsin-sulfite solution. From day to day the strength of the fuchsin-sulfite solution changed due to the sulfuric acid formed by the oxidation of the sulfur dioxide. This effect decreased the sensitiveness of the solution so greatly that it was prepared fresh at the end of ten days. The solution was stored in a one-quart, brown glass, beer bottle at all times. Those factors which change the composition of the solution certainly caused a comparative difference in the magenta color developed and consequently gave different potentiometer scale readings from day to day for the same aldehyde content. During the short period of time for any one investigation the composition changes of the fuchsin-sulfite solution were so slight that its effect would not show up in the data. Therefore, relative effects caused by ultrasonic irradiation on the given mixture would be ascertained with a reasonable degree of accuracy. When the fuchsin-sulfite solution was not in use, it was kept in the dark in a water bath at approximately 4°C.

From the standpoint of economy in the use of reagents, a diluted ethyl alcohol-hydrogen peroxide-water mixture was prepared as follows for further investigation: Assuming the reaction,



the weight requirement of hydrogen peroxide for a given weight of ethyl alcohol was calculated on a 100 per cent basis as previously shown. The desired acetaldehyde standard was added and thoroughly mixed with the solution. Five ml of this mixture was pipeted into a 50 ml glass stoppered volumetric flask. This was diluted to the mark with distilled water, stoppered, and shaken until thoroughly mixed. A 5 ml portion of this diluted mixture was pipeted into a 100 ml beaker. Twenty five ml of 50 per cent ethyl alcohol was added which had been maintained at 15°C. Ten ml of fuchsin-sulfite solution was added which had also been maintained at 15°C. This mixture was gently shaken and 20 ml was poured into a 25 mm x 150 mm OD pyrex lipless test tube and stoppered with a number 7 cork. The tube was placed in a test tube rack for 15 minutes at room temperature (28°C). The portion not poured into the test tube was left in the beaker, but kept in a water bath for 15 minutes at 15°C. The data for the tests at 15°C and 28°C are shown in Table IV. Figure 26 is a plot of these data and clearly shows that temperature has an effect on the development of the magenta color. It may also be seen that the data gives a straight line relationship on ordinary coordinate paper (Semilog paper need not be used since the scale divisions on the colorimeter are logarithmic and not linear). This observation

TABLE IV

Experimental Data For The Development Of A Colorimetric Quantitative Method For Acetaldehyde Determination At 15°C and 28°C In An Ethyl Alcohol-Hydrogen Peroxide-Water Mixture Using The Volume Requirements Of Reagents For The AOAC Colorimetric Method Corrected For The Volume Of 50 Per Cent Ethyl Alcohol In The Standard Acetaldehyde Solution.

Ethyl Alcohol-Hydrogen Peroxide-Water Mixture ml	Standard Acetaldehyde Solution 1 ml = 0.0002 gm Acetaldehyde ml	50 Per Cent Ethyl Alcohol ml	Fuchsin-Sulfite Solution ml	Potentiometer Scale Reading	
				15°C	28°C
5	0	25	10	22	29
5	2	23	10	23.5	31.5
5	4	21	10	24	34
5	6	19	10	25.5	36.5
5	10	15	10	23	42
5	14	11	10	30	46
5	18	7	10	33	50
5	20	5	10	33.5	52

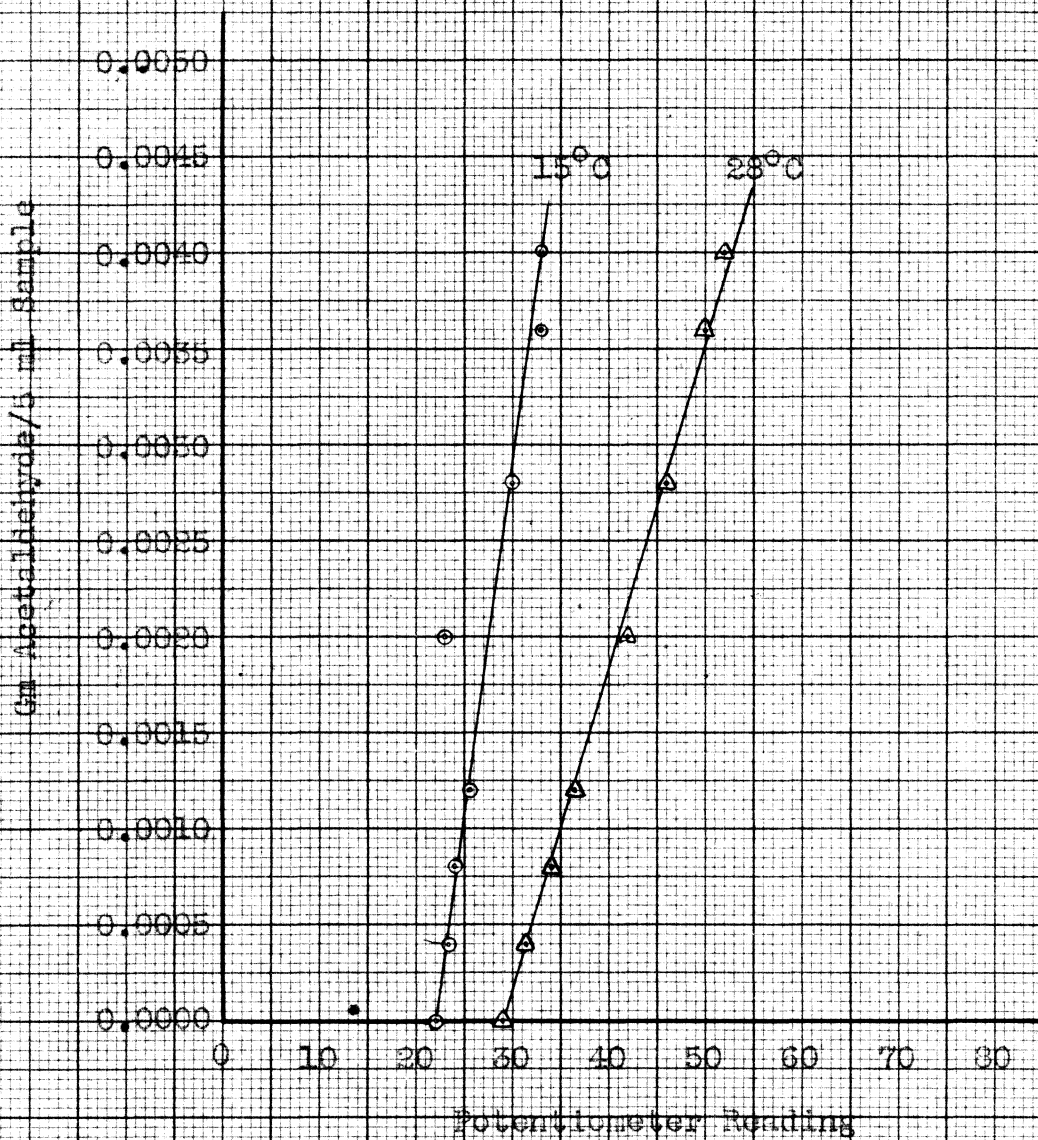


Figure 26

Results of Determination of Acetaldehyde at 15°C and 28°C Using Klett-Summerson Photoelectric Colorimeter on an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture and the Volume Requirements of Reagents for the AOAC Colorimetric Method Corrected for the Volume of 50 Per Cent Ethyl Alcohol in the Standard Acetaldehyde Solution.

agrees with Yoe's (212) statement that the "color developed is not in direct proportion to the amount of aldehyde present," but the logarithm of the intensity of the color developed versus aldehyde present does give a straight line.

By examining the curves on the figures referred to, it is believed safe to assume that the color intensity development of the fuchsin-sulfite solution and the ethyl alcohol-hydrogen peroxide-water mixture are in close proportion to the amount of aldehyde present and follow a straight line relationship. Human and experimental error may be as much as plus or minus two scale divisions on the colorimeter.

In order to fix a temperature for the development of the magenta color, 30°C was chosen. At this temperature a comparatively good color should be developed which will give desirable potentiometer scale readings on the colorimeter. Data for preliminary experimental work using this temperature on solutions prepared as above are shown in Table V. Figure 27 is a plot of this data which again shows the straight line relationship between aldehyde content and potentiometer readings.

As a result of this work, the following procedure was established for acetaldehyde in this investigation: Five ml of the ethyl alcohol-hydrogen peroxide-water mixture to be analyzed was pipeted into a 50 ml glass stoppered volumetric flask and filled to the mark with distilled water, stoppered and shaken until thoroughly mixed. A 5 ml portion of this diluted mixture was

TABLE V

Experimental Data For The Development Of A Colorimetric Quantitative Method For Acetaldehyde Determination At 30°C In An Ethyl Alcohol-Hydrogen Peroxide-Water Mixture Using The Volume Requirements Of Reagents For The AOAC Colorimetric Method Corrected For The Volume Of 50 Per Cent Ethyl Alcohol In The Standard Acetaldehyde Solution.

Ethyl Alcohol-Hydrogen Peroxide-Water Mixture	Standard Acetaldehyde Solution 1 ml = 0.0002 gm Acetaldehyde	50 Per Cent Ethyl Alcohol	Fuchsin-Sulfite Solution	Potentiometer Scale Reading
ml	ml	ml	ml	
5	0	25	10	31
5	2	23	10	32.5
5	4	21	10	36
5	6	19	10	38
5	10	15	10	43
5	14	11	10	47.5
5	18	7	10	52
5	20	5	10	55

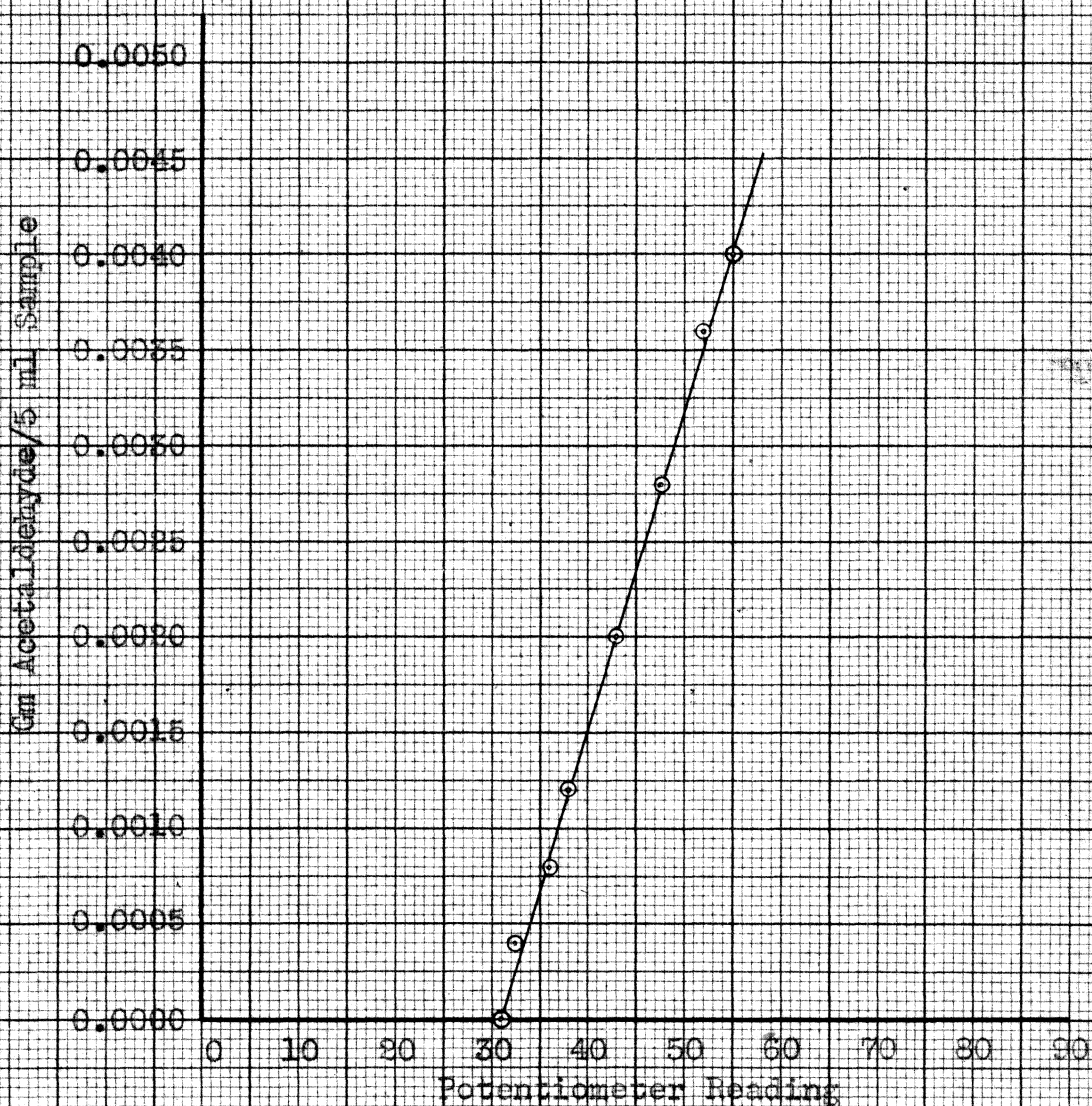


Figure 27

Results of Determination of Acetaldehyde at 30°C Using Klett-Summerson Photoelectric Colorimeter on an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture and the Volume Requirements of Reagents for the AGAC Colorimetric Method Corrected for the Volume of 50 Per Cent Ethyl Alcohol in the Standard Acetaldehyde Solution.

pipeted into a 100 ml beaker. Immediately 25 ml of a 50 per cent by volume ethyl alcohol-water mixture was added which had been maintained at 15°C. Ten ml of fuchsin-sulfite solution which had been maintained at 15°C was immediately added. This mixture was gently shaken and poured into a 25 mm x 150 mm OD lipless pyrex test tube until nearly full and then stoppered with a number 7 cork. The tube was placed in a water bath and kept at 30°C for 15 minutes. The relative aldehyde content in 10 ml of this mixture was determined by using a Klett-Summerson Photoelectric Colorimeter.

3. pH And "Acid" Content

Qualitative. One of the most sensitive qualitative tests for acetic acid located in the literature search was a method described by Treadwell and Hall (198) and Feigl (74). These authors state that when lanthanum nitrate is mixed with iodine and ammonia in the presence of acetic acid or alkali acetates under suitable conditions, a dark blue precipitate results. It is explained that this coloration is probably due to the adsorption of iodine on the basic lanthanum acetate.

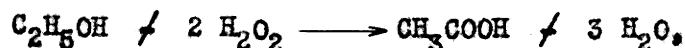
"Nitrates, chlorides, bromides, and iodides do not interfere with the detection of small amounts of acetate, even when present in 30 to 40 times excess, but they weaken the intensity of the blue color. Sulfates, however, interfere in relatively small amounts, and

similarly all anions that form insoluble salts with lanthanum (e.g., phosphates), and all cations that give precipitates with ammonia."

Due to the purity of the reagents used in this investigation no trouble should be experienced by interfering substances. This was further borne out by the fact that when the reagents to be tested were treated with barium chloride, no precipitate of barium sulfate was noted.

The method followed for preliminary investigation was to "place 1 drop of the solution to be tested on a spot plate and add 1 drop of 5 per cent lanthanum nitrate solution and 1 drop of 0.01 N iodine solution. After a minute add 1 drop of 1 N ammonium hydroxide and allow to stand for a few minutes." According to Feigl this method will detect 50 micrograms of acetic acid.

Considering the equation,



a mixture of ethyl alcohol-hydrogen peroxide-water was prepared on the basis of previous calculations already shown. A drop of this mixture was tested for acetates. It was observed that on addition of iodine a liberation of gas bubbles occurred. With increasing time, the rate of gas evolution increased with a decrease in the color intensity of the iodine solution. It was also observed that on adding the ammonium hydroxide, the color of the iodine disappeared completely, giving a colorless solution with a large volume of gas evolution.

Since hydrogen peroxide is slightly acid by its own nature, it is not understood why the iodine color disappeared. Even if iodic acid were formed, Bancroft and Murphy ⁽⁶⁾ state that 30 per cent hydrogen peroxide reduces it to iodine which should give a coloration in the solution. They found that with even M/2000 iodic acid, 30 per cent hydrogen peroxide gave a pink color due to iodine when carbon tetrachloride was present.

With this difficulty, the lanthanum nitrate test was unsatisfactory unless some means were devised to prevent the undesired reactions. In order to further study this method the following preliminary investigations were made:

a. Volumes of reagents required for the test were varied with negative results observed.

b. Sodium acetate was dissolved in the ethyl alcohol-hydrogen peroxide-water mixture and the whole tested for acetates. Results were negative.

c. An ethyl alcohol-water mixture was tested for acetates, but no blue color formation was observed.

d. The ethyl alcohol-hydrogen peroxide-water mixture was made slightly alkaline with sodium hydroxide and the whole evaporated to dryness over a water bath. On testing for acetates a positive test was observed. The question arose as to whether the liberation of oxygen during evaporation caused some oxidation of the ethyl alcohol since the sodium hydroxide

and other reagents used in the test gave negative results for acetates. Since this question could not readily be answered the lanthanum nitrate method was abandoned.

A ferric chloride test as given by Feigl ⁽⁷³⁾ was considered. In this method, a drop of the acetate solution was neutralized by heating with calcium carbonate. When ferric chloride solution is added a red-brown complex iron acetate is formed if acetates are present. Feigl reports this method is sensitive to 10 micrograms of acetic acid. Ethyl alcohol-hydrogen peroxide-water mixtures were tested with and without the known presence of acetate. In both cases using this method, no apparent color change was observed. In one case where volumes greater than a drop were used the whole mass became boiling hot after the addition of the ferric chloride solution. Because of these results, the ferric chloride method was abandoned and no further qualitative methods considered.

Quantitative. It was originally planned to determine the quantity of acetic acid present by titrating with sodium hydroxide using phenolphthalein as an indicator.

Since it was known that only small amounts of acetic acid would be originally present in the ethyl alcohol, a 0.01 N sodium hydroxide solution was prepared. To a sample of the ethyl alcohol-hydrogen peroxide-water mixture to be titrated a drop of phenolphthalein indicator was added. It was observed that the 0.01 N sodium hydroxide solution was so weak that a sharp color change could not be seen. Consequently, the normality of the sodium hydroxide was made

0.1 N since Pierce and Haenisch (150) state that a titration is not feasible if the volume of the reagent required to change the pH sufficiently to cause a sharp indicator color change is greater than 0.1 - 0.2 ml. No change in the selection of the indicator should be made since the pH range of suitable indicators for acetic acid titration with sodium hydroxide is restricted to the region 7.5 - 10.

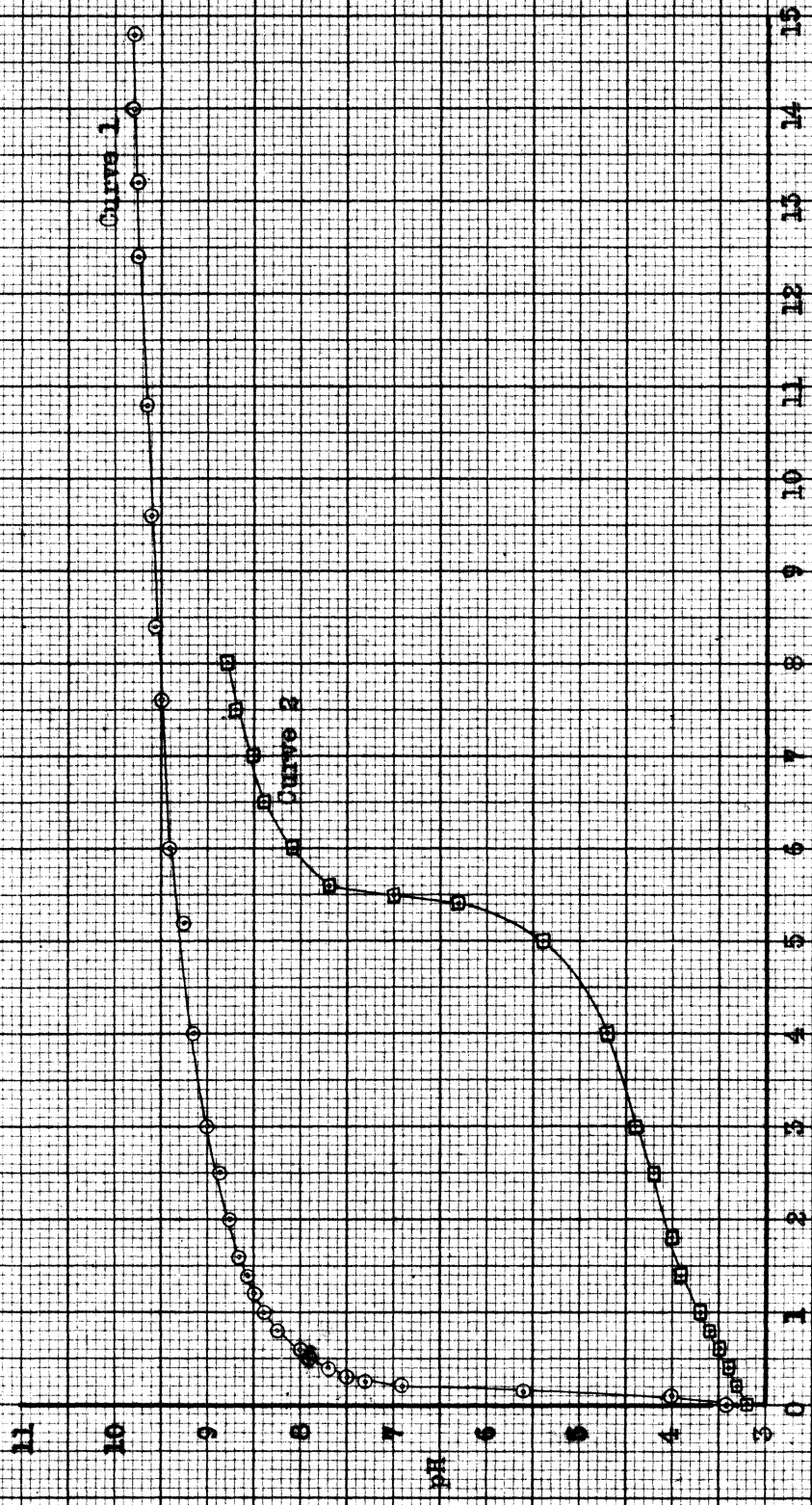
On further work using the 0.1 N sodium hydroxide it was observed that the hydrogen peroxide in the mixture being titrated had a tendency to "bleach" the phenolphthalein. In order to observe the indicator color change more easily, a preliminary investigation was made using the following procedure: A blank was made on 15 ml of distilled water containing 3 drops of 1 per cent phenolphthalein and titrated with 0.1 N sodium hydroxide. Pipet 5 ml of the sample to be tested into 15 ml of distilled water. Add 3 drops of 1 per cent phenolphthalein and titrate with 0.1 N sodium hydroxide using a microburet. For a container, a glass vial was chosen whose capacity was 35 ml, length 10 cm, outside diameter 2.5 cm, and with a flat bottom. This vial serves the purpose of a color comparator tube. Therefore, the pink color of the indicator at the end point should be easily seen when the tube is compared with a similar tube filled with 20 ml of distilled water. At all times while titrating, the glass vials were placed on a sheet of white paper and the whole illuminated by a daylight type fluorescent light.

At first, this method seemed satisfactory but duplicate titrations were found to deviate as much as plus or minus 0.2 ml on the

microburet. This magnitude was considered too great for the purposes of this investigation. In all probability the error produced was primarily due to the "bleaching" effect of the hydrogen peroxide on the phenolphthalein while the titration was being carried out. It was observed that when an excess of sodium hydroxide was added, the red color faded in a relatively short time until the solution was again colorless.

Resort was made to a Beckman glass electrode pH meter. Curve number 1 on figure 28 shows a titration curve on 5 ml of ethyl alcohol-hydrogen peroxide-water mixture and 50 ml of distilled water using 0.1 N sodium hydroxide. It may be seen that no sharp deflection was noted, so in order to determine the final pH value in which to titrate assuming acetic acid was present, 5 ml of 0.1 N acetic acid was added to 5 ml of the sample and 45 ml of distilled water. Curve number 2 on figure 28 shows that the end point of the titration should be at a pH of approximately 7.

The procedure for the pH and "acid" content adopted for this investigation was to standardize a Beckman glass electrode pH meter with a buffer solution of $\text{pH} = 7.07 \pm 0.04$ at 25°C . Five ml of the ethyl alcohol-hydrogen peroxide-water mixture was pipeted into a 100 ml beaker and diluted with 50 ml of distilled water. It was then stirred until thoroughly mixed with a glass rod, keeping the temperature as close to 25°C as practicable. The pH of the mixture was determined and then the mixture was titrated with 0.1 N sodium hydroxide using a microburet until a pH of 7.0 was reached.



MILLILITERS OF 0.0981 N SODIUM HYDROXIDE

FIGURE 23

Determination of Optimum pH for the Determination of the Acid Content in Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures Using a Beckman pH Meter

E. Data And Results

Tables VI through Table XIII are a compilation of the data for 400 kc, 700 kc, 1000 kc, and 1500 kc ultrasonic irradiation on ethyl alcohol-hydrogen peroxide-water mixtures for one minute and twenty minutes respectively.

pH. Figures 29a, 29b, 29c, 29d, 29e, 29f, 29g, and 29h are a graphical representation of the data shown in Tables VI through Table XIII for the effect of ultrasonic irradiation on the pH of an ethyl alcohol-hydrogen peroxide-water mixture as the intensity of the oscillations were increased due to an increase of the voltage applied to the quartz crystal oscillator.

Acid Content. Figures 30a, 30b, 30c, 30d, 30e, 30f, 30g, and 30h are a graphical representation of the data shown in Tables VI through Table XIII for the effect of ultrasonic irradiation on the acid content of an ethyl alcohol-hydrogen peroxide-water mixture as the intensity of the oscillations were increased due to an increase of the voltage applied to the quartz crystal oscillator. The acid content of the mixture was based on the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 using a Beckman pH meter.

Acetaldehyde. Figures 31a, 31b, 31c, 31d, 31e, 31f, 31g, and 31h are a graphical representation of the data shown in Tables VI through Table XIII for the effect of ultrasonic irradiation on the apparent acetaldehyde content of an ethyl alcohol-hydrogen peroxide-

water mixture as the intensity of the oscillations were increased due to an increase of the voltage applied to the quartz crystal oscillator. The apparent acetaldehyde content of the mixture was based on the potentiometer readings of a Klett-Summerson Photoelectric Colorimeter.

Hydrogen Peroxide. Figures 32a, 32b, 32c, 32d, 32e, 32f, 32g, and 32h are a graphical representation of the data shown in Tables VI through Table XIII for the effect of ultrasonic irradiation on the hydrogen peroxide content of an ethyl alcohol-hydrogen peroxide-water mixture as the intensity of the oscillations were increased due to an increase of the voltage applied to the quartz crystal oscillator. The hydrogen peroxide content of the mixture was based on the volume of 0.0990 N potassium permanganate solution required to titrate the hydrogen peroxide in the mixture.

Relative Composition Changes. Tables XIV through Table XXI are a compilation of the relative composition changes of an ethyl alcohol-hydrogen peroxide-water mixture due to ultrasonic irradiation from the composition of an ethyl alcohol-hydrogen peroxide-water mixture not subjected to ultrasonic irradiation.

TABLE VI

400 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for One Minute

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N KMnO_4
Number	Dial Reading	Dial Reading	v	ma	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	58	58	62	62	3.3	0.25	31	15.45
2	14	40.5	200	30	58	58	62	62	3.1	0.28	30	15.55
3	27	40.5	400	52	58	58	62	62	2.9	0.30	31	15.44
4	38	40.5	600	100	58	58	62	62	3.1	0.29	31	15.40
5	50	40.5	800	140	58	58	62	62	2.8	0.32	30	15.52
6	60	40.5	1000	170	58	58	62	62	2.9	0.30	31	15.47
7	71	40.5	1200	190	58	58	62	62	2.9	0.30	30	15.53
8	82	40.5	1400	240	58	58	62	62	2.9	0.30	30	15.50
9	91	40.5	1600	270	58	58	62	62	2.9	0.30	30	15.52
10	103	40.5	1800	303	58	58	62	62	3.1	0.29	31	15.40
11	115	40.5	2000	360	58	58	62	62	3.2	0.27	30	15.45

Remarks: Blank on 3 ml of concentrated sulfuric acid and 75 ml of distilled water was 0.03 ml of 0.0990 N KMnO_4 . Recommend equipment not be operated over 1800 volts as the amperage fluctuated too much above this voltage. Mixture being irradiated was in a violent state of turbulence at 2000 volts. Gas bubbles were observed in the mixture while being irradiated at all voltages. Hydrogen peroxide used was lot number 43357 from bottle numbered 3 for this investigation.

TABLE VII

400 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for Twenty Minutes

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N KMnO ₄
Number	Dial Reading	Dial Reading	v	ma	°f	°f	°f	°f	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	57	57	64	60	3.3	0.29	31	15.46
2	15	39	200	30	57	57	64	60	3.1	0.25	33	15.54
3	26	42	400	55	57	57	64	60	3.15	0.24	33	15.52
4	38	42	600	95	58	58	65	61	3.1	0.25	32	15.45
5	48	42	800	135	58	58	65	61	3.2	0.26	31	15.40
6	60	42	1000	160	58	58	66	61	3.7	0.24	30	15.45
7	71	42	1200	190	57	57	67	61	3.9	0.18	30	15.36
8	85	42	1400	240	57	57	67	61	3.6	0.19	29	15.47
9	93	40.5	1600	270	58	58	72	63	3.6	0.23	29	15.44
10	105	40.5	1800	310	57	57	74	64	3.7	0.24	30	15.50

Remarks: Fog noticed over mixture in reaction tube at 1000 volts and above. At 1000 volts and above, the liquid in the reaction tube was in a violet state of turbulence. Small gas bubbles were observed in the mixture while being irradiated at all voltages. Hydrogen peroxide used was lot number 43357 from bottle numbered 3 for this investigation.

TABLE VIII

700 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for One Minute

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N K_2O_4
Number	Dial Reading	Dial Reading	v	ma	$^{\circ}F$	$^{\circ}F$	$^{\circ}F$	$^{\circ}F$	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	57	57	64	60	4.2	0.10	32	15.65
2	13	40.5	200	30	57	57	64	60	3.8	0.12	31	15.98
3	26	40.5	400	60	58	58	64	60	4.2	0.10	30	15.76
4	39	40.5	600	90	58	58	64	60	3.9	0.11	30	15.73
5	49	40.5	800	130	58	58	67	62	4.7	0.05	29	15.60
6	60	40.5	1000	170	58	58	64	60	4.8	0.07	33	15.62
7	71	40.5	1200	190	58	58	64	60	4.6	0.08	32	15.78
8	82	40.5	1400	250	58	58	64	60	4.8	0.07	30	15.75
9	91	40.5	1600	265	58	58	63	60	4.4	0.10	32	15.70
10	103	40.5	1800	305	58	58	63	60	4.3	0.10	32	15.70

Remarks: The oil temperature was higher at 800 volts because the equipment was not in operation during the lunch hour. Small gas bubbles were observed in the mixture being irradiated at all voltages. Hydrogen peroxide used was lot number 40903 from bottle numbered 4 for this investigation.

TABLE IX

700 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for Twenty Minutes

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N KMnO_4
Number	Dial Reading	Dial Reading	v	ma	°F	°F	°F	°F	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	56	56	64	60	4.1	0.12	32	15.76
2	14	40.5	200	30	56	56	64	60	3.9	0.10	31	15.73
3	28	40.5	400	70	56	57	66	62	4.0	0.10	31	15.76
4	39	40.5	600	95	56	57	68	62	4.0	0.14	38	15.80
5	50	40.5	800	130	58	58	68	62	3.7	0.15	35	15.71
6	61	40.5	1000	175	58	58	70	63	3.9	0.10	37	15.78
7	71	40.5	1200	180	57	57	70	63	3.7	0.15	34	15.58
8	81	40.5	1400	225	57	57	72	63	3.8	0.15	30	15.61
9	91	40.5	1600	270	57	57	73	64	4.0	0.10	32	15.75
10	103	40.5	1800	305	58	58	75	65	4.0	0.10	32	15.50

Remarks: At 1000 volts and above the mixture in the reaction tube was in a violent state of turbulence. Small gas bubbles were observed in the mixture being irradiated at all voltages. In runs 4, 5, and 6 the potentiometer reading increased sharply. A blank run was made to determine if any reagents had been accidentally contaminated. This was apparently not the case since a potentiometer reading of 31 was observed. Hydrogen peroxide used was lot number 40908 from bottle numbered 4 for this investigation.

TABLE X

1000 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for One Minute

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N KMnO ₄
Number	Dial Reading	Dial Reading	v	ma	°f	°f	°f	°f	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	57	57	68	64	4.1	0.09	39	15.54
2	13	59	200	30	57	57	68	64	4.1	0.13	44	15.48
3	26	59	400	60	56	56	64	61	3.9	0.12	47	15.80
4	38	59	600	95	56	56	64	61	3.8	0.13	48	15.52
5	49	59	800	130	56	56	64	61	3.7	0.14	46	15.46
6	60	59	1000	165	56	56	64	61	3.6	0.15	39	15.64
7	71	59	1200	195	56	56	46	61	3.6	0.15	41	15.36
8	81	59	1400	230	56	56	46	61	3.6	0.15	47	15.53
9	91	59	1600	260	56	56	46	61	3.7	0.15	48	14.45
10	104	59	1800	320	56	56	46	61	3.7	0.14	39	15.43

Remarks: Dense fog formed over mixture in reaction tube at 800 to 1800 volts. Small gas bubbles were observed in the mixture while being irradiated at all voltages. Hydrogen peroxide used was lot number 40908 from bottle numbered 5 for this investigation.

TABLE XI

1000 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for Twenty Minutes

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0999 N KMnO ₄
Number	Dial Reading	Dial Reading	v	ma	°F	°F	°F	°F	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	56	56	64	61	4.0	0.10	41	15.50
2	15	59	200	25	56	56	64	61	3.9	0.12	45	15.60
3	27	59	400	65	56	56	64	61	3.9	0.12	45	15.58
4	39	59	600	95	56	56	65	61	3.9	0.12	41	15.55
5	50	59	800	125	55	55	64	60	4.0	0.11	35	15.55
6	60	59	1000	160	55	55	65	60	4.0	0.12	34	15.48
7	71	59	1200	200	55	55	65	60	4.0	0.12	37	15.47
8	80	59	1400	225	55	55	65	60	3.8	0.14	33	15.45
9	91	59	1600	260	55	55	65	60	3.8	0.14	33	15.44
10	105	59	1800	325	55	55	65	60	3.7	0.15	41	15.41

Remarks: During 200 volt run, small gas bubbles were slowly emitted from the mixture in the reaction tube. These bubbles resonated in the nodes of the ultrasonic waves and eventually traveled to the surface of the mixture and burst. At 400 volt and 600 volt runs the gas bubbles continued to be emitted at an apparently constant rate. At 800 volts and above intense fog formed over the mixture in the reaction tube. At 600 volts and above the gas bubbles noticed previously continued to be emitted, but their diameter was increased to about 1/8 inch. The bubbles resonated in the nodes of the ultrasonic waves and slowly rose to the surface of the mixture and burst. Hydrogen peroxide used was lot number 40908 from bottle numbered 5 for this investigation.

TABLE XII

1500 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for One Minute

Run	Powerstat	Impedance	Voltage	Ampereage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N KMnO ₄
Number	Dial Reading	Dial Reading	v	ma	°F	°F	°F	°F	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	54	54	62	59	3.9	0.11	37	15.60
2	13	27	200	30	54	54	62	59	4.0	0.11	39	15.58
3	26	27	400	60	54	54	62	59	3.8	0.12	40	15.56
4	38	27	600	100	54	54	62	59	3.75	0.12	38	15.63
5	49	27	800	120	54	54	62	59	3.7	0.15	35	15.67
6	59	27	1000	165	54	54	62	59	3.75	0.12	35	15.65
7	72	27	1200	200	54	54	62	59	3.75	0.12	35	15.65
8	81	27	1400	235	54	54	62	59	3.8	0.11	35	15.61
9	92	27	1600	250	54	54	62	59	3.8	0.12	35	15.54
10	104	27	1800	290	54	54	62	59	3.8	0.12	35	15.50

Remarks: At 200 volts very small gas bubbles were seen in the mixture in the reaction tube, but all remained stationary. At 400 volts very small bubbles formed which slowly rose to the surface of the mixture and burst. At 800 volts fewer gas bubbles were emitted, but their diameters were larger. At 1000 volts, the bubbles formed appear to have larger diameters than the bubbles formed at 800 volts. At 1400 volts, a fog was formed with more gas bubbles. At 1600 volts, few gas bubbles were noticed but the intensity of the fog increased. At 1800 volts, fewer gas bubbles were noticed but the fog was very intense. Hydrogen peroxide used was lot number 40908 from bottle numbered 6 for this investigation.

TABLE XIII

1500 kc Ultrasonic Irradiation on Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures for Twenty Minutes

Run	Powerstat	Impedance	Voltage	Amperage	Water to Cooler	Water from Cooler	Oil to Cooler	Oil from Cooler	pH	Acid Content 0.0981 N NaOH	Acetaldehyde Content	Hydrogen Peroxide 0.0990 N KMnO ₄
Number	Dial Reading	Dial Reading	v	ma	°F	°F	°F	°F	Scale Reading	ml	Potentiometer Reading	ml
1	0	0	0	0	54	54	61	58	3.9	0.10	37	15.63
2	13	27	200	45	54	54	61	58	3.85	0.11	35	15.83
3	27	27	400	70	54	54	61	58	3.8	0.12	34	15.76
4	39	27	600	100	54	54	61	58	3.65	0.13	37	15.62
5	50	27	800	130	54	54	62	58	3.6	0.14	40	15.60
6	61	27	1000	160	54	54	62	59	3.5	0.16	38	15.52
7	72	27	1200	190	54	55	63	59	3.55	0.15	37	15.50
8	81	27	1400	220	54	55	64	59	3.5	0.16	37	15.40
9	93	27	1600	240	54	55	64	59	3.5	0.16	36	15.50
10	104	27	1800	250	54	55	65	60	3.6	0.15	37	15.60

Remarks: At 200 volts no gas bubbles formed. At 400 volts many small gas bubbles evolved and rose to the surface of the mixture and burst. At 600 volts many small gas bubbles evolved which also rose and burst. As the voltage was increased from 800 to 1000 volts the same phenomenon was noticed, except the diameter of the bubbles increased as the voltage increased. As the voltage was increased from 1000 volts to 1800 volts fog was produced which increased in density as the voltage increased. Hydrogen peroxide used was lot number 40908 from bottle numbered 6 for this investigation.

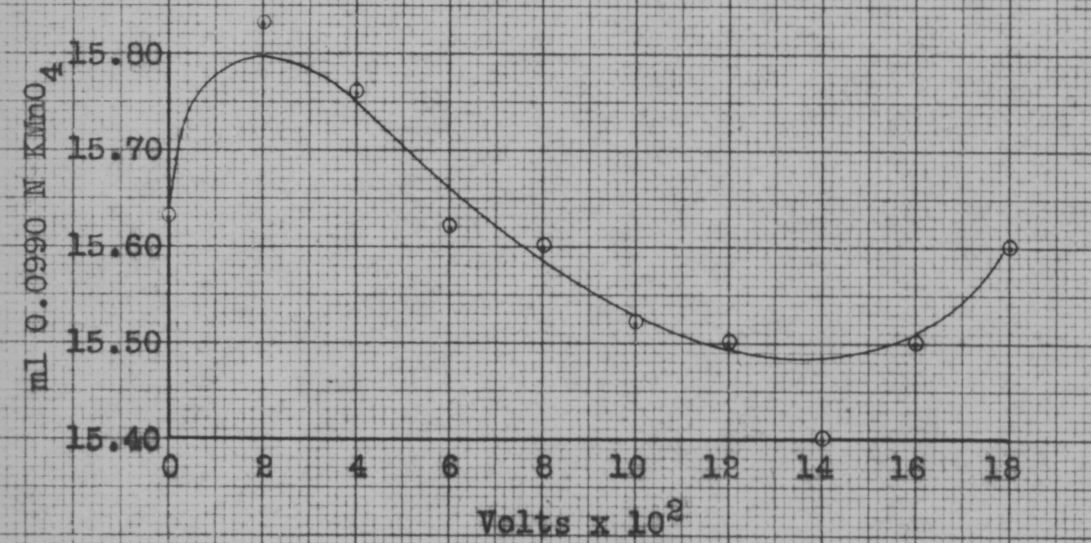
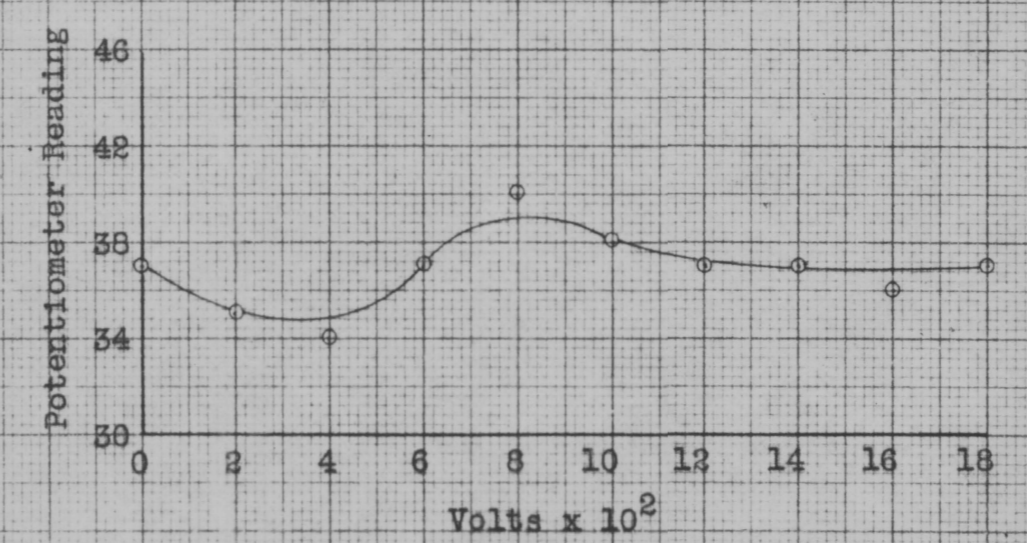
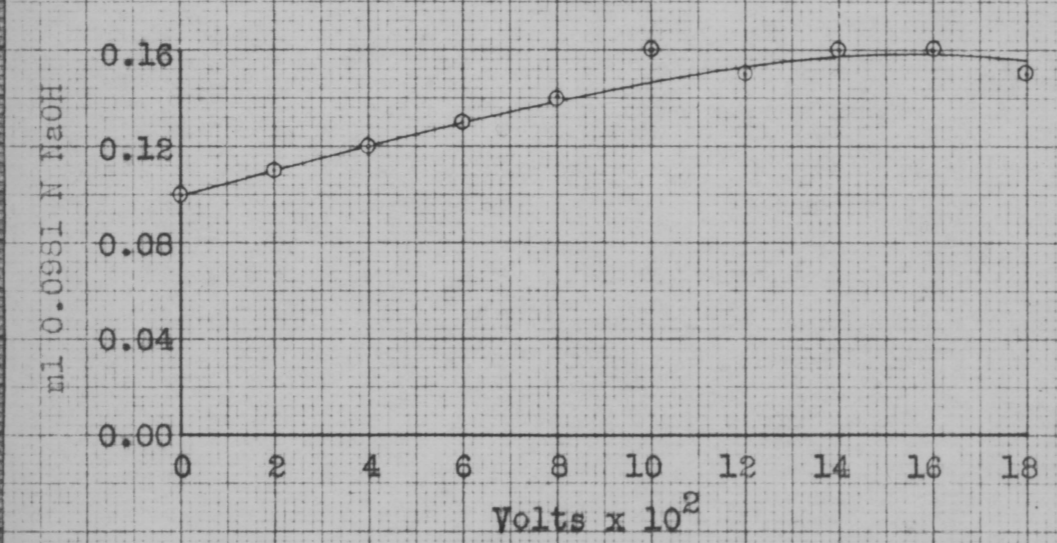
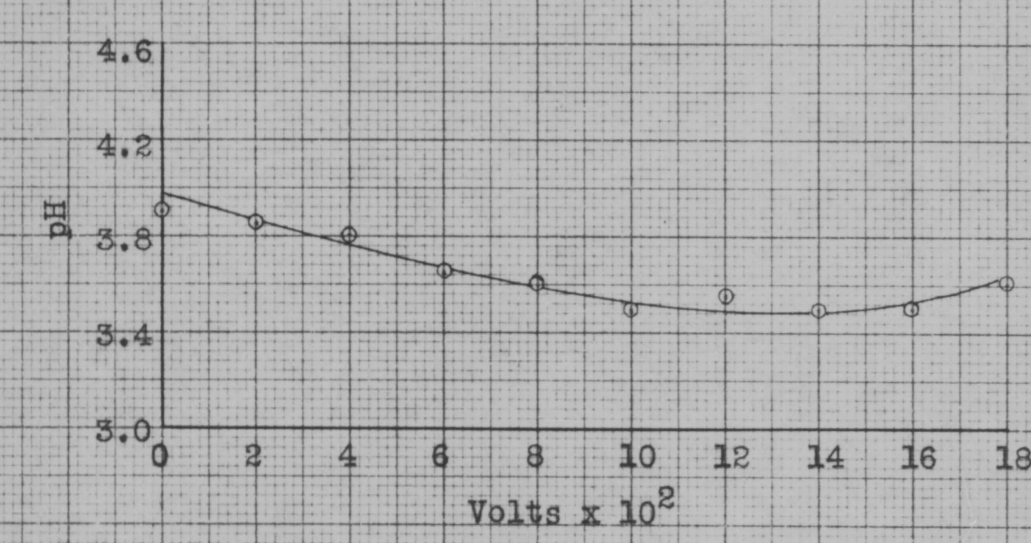
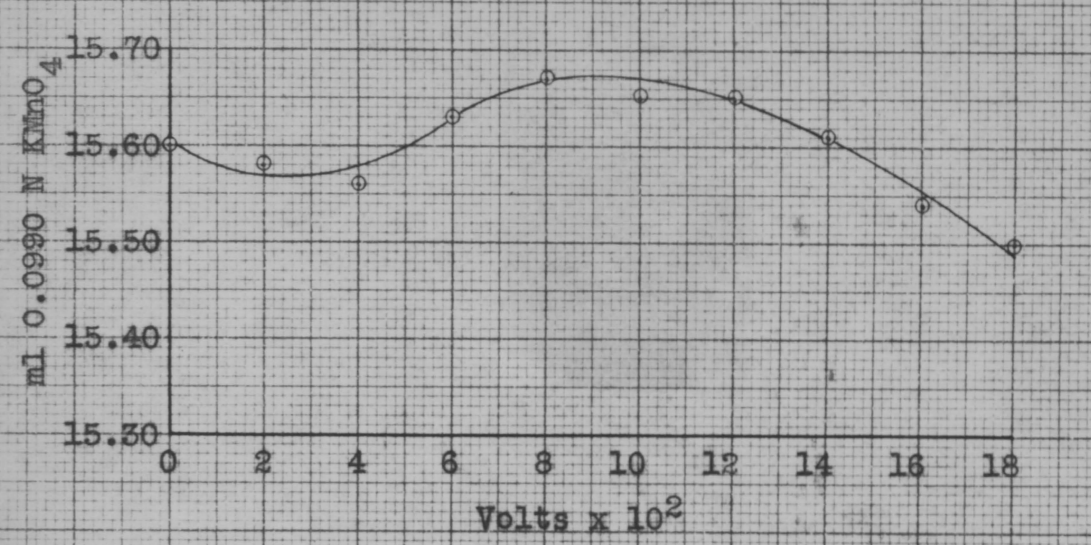
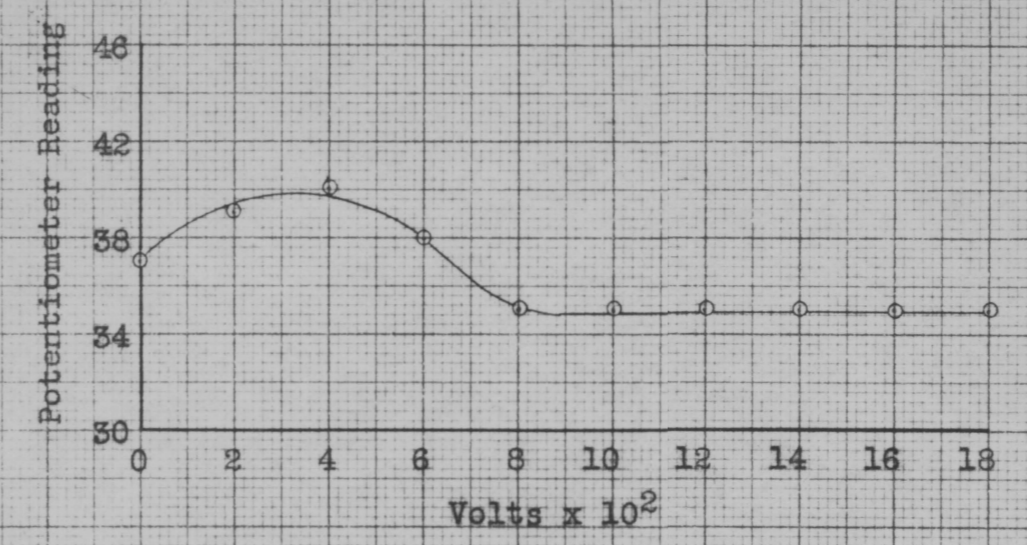
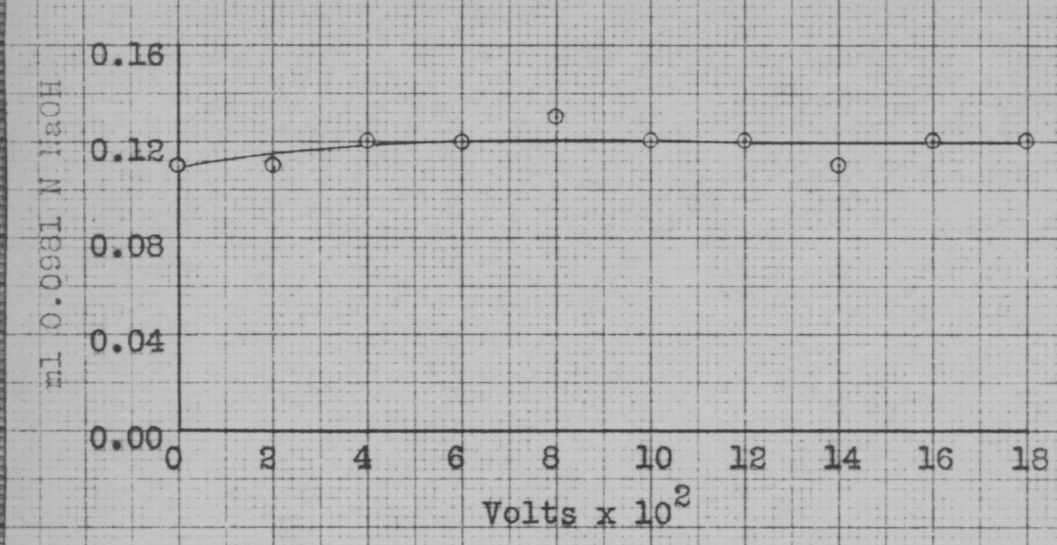
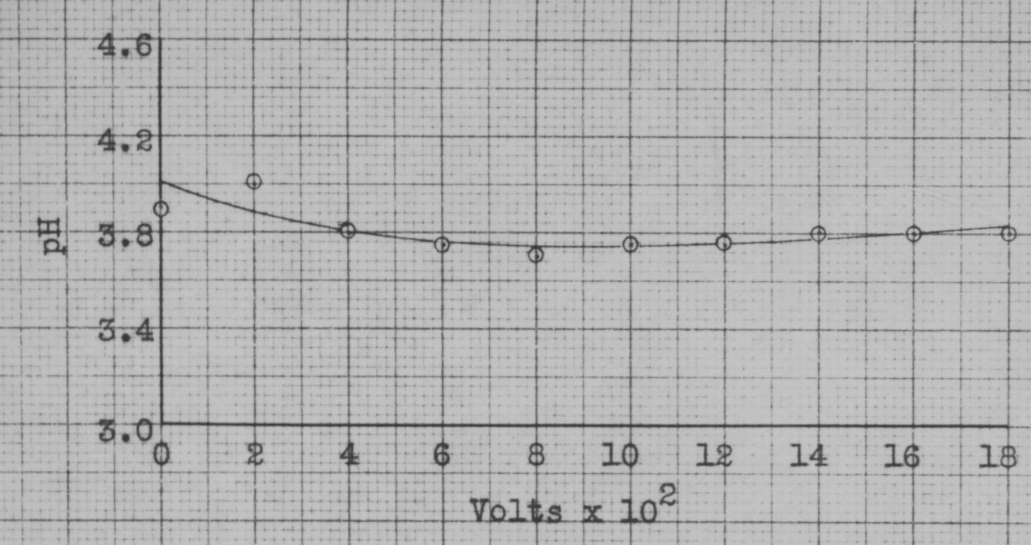
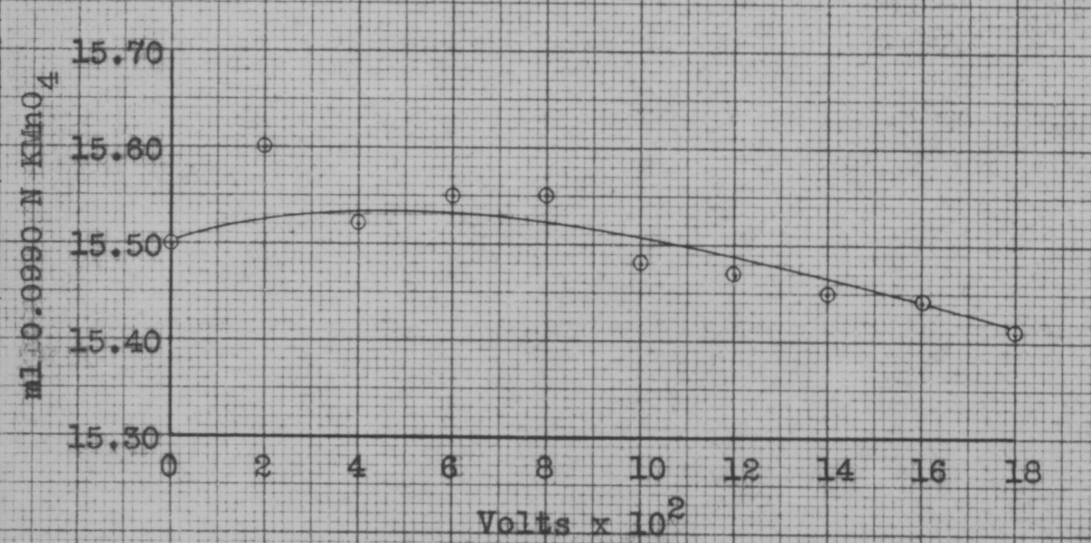
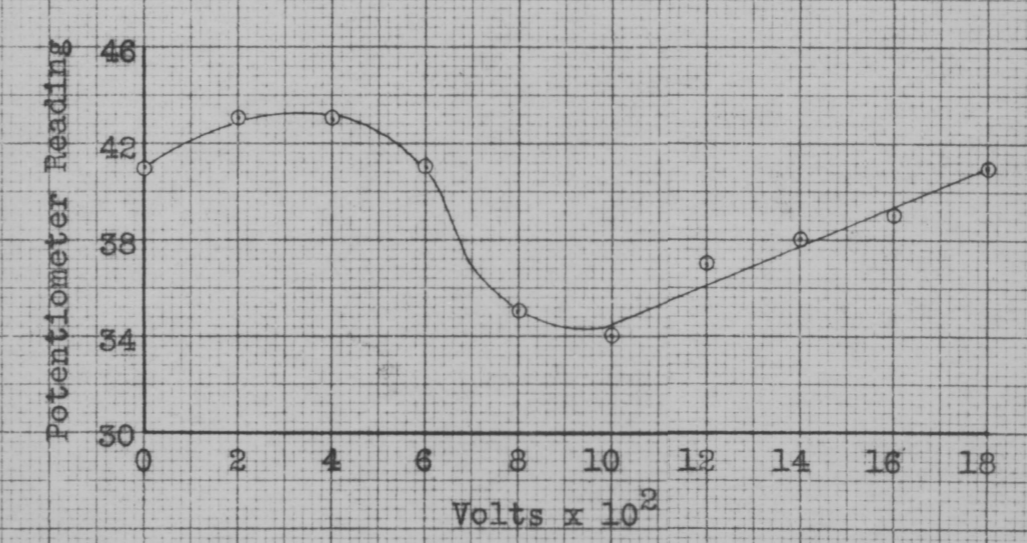
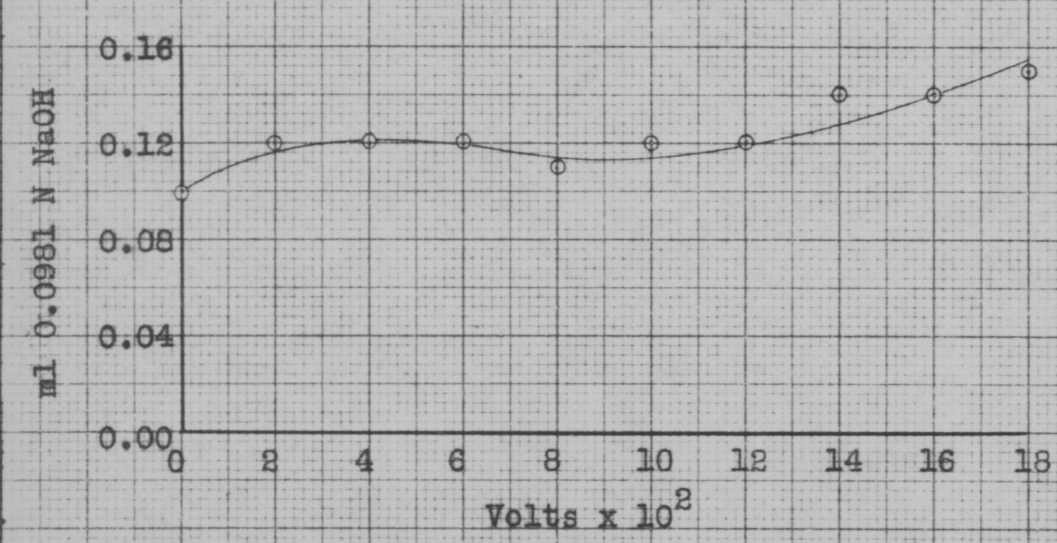
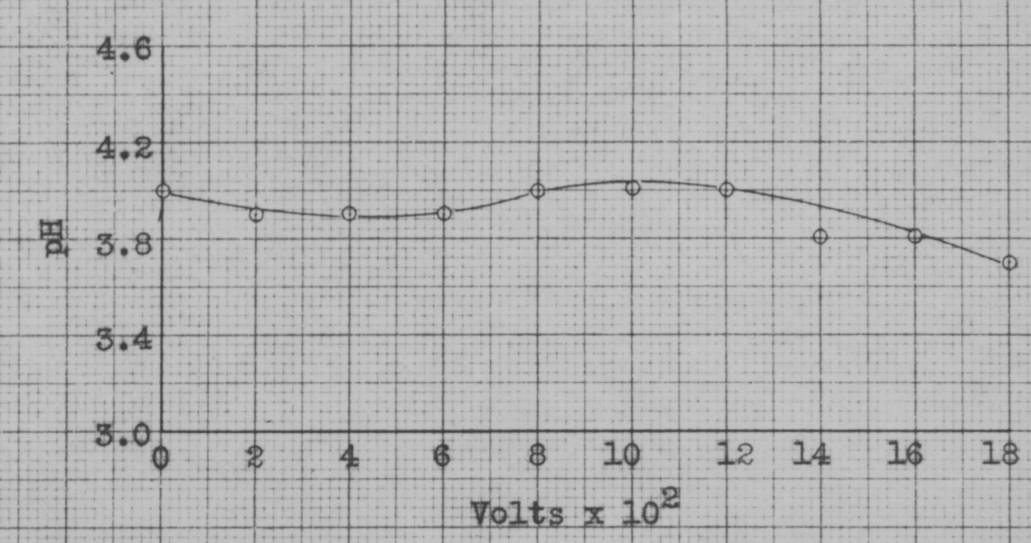
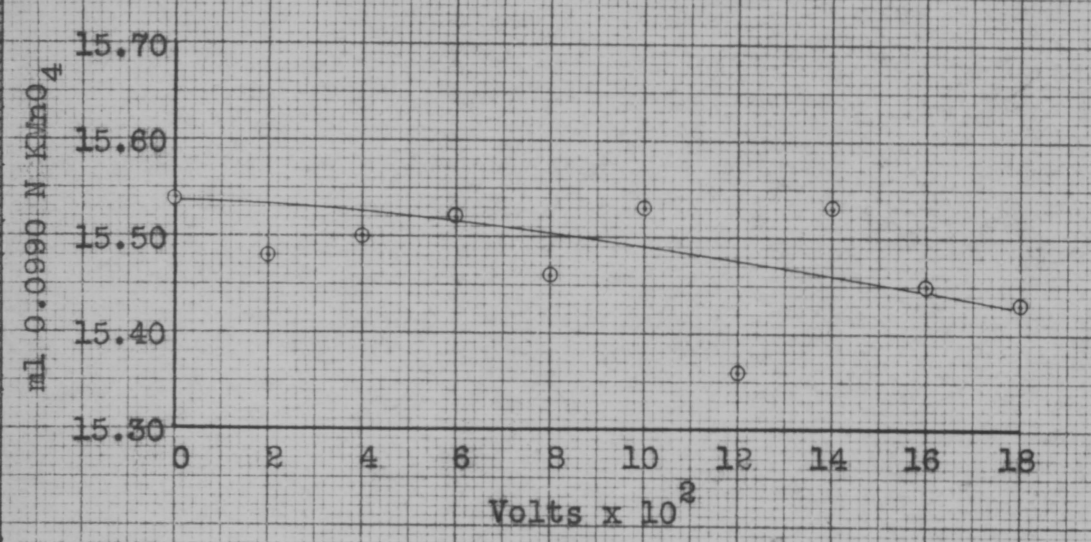
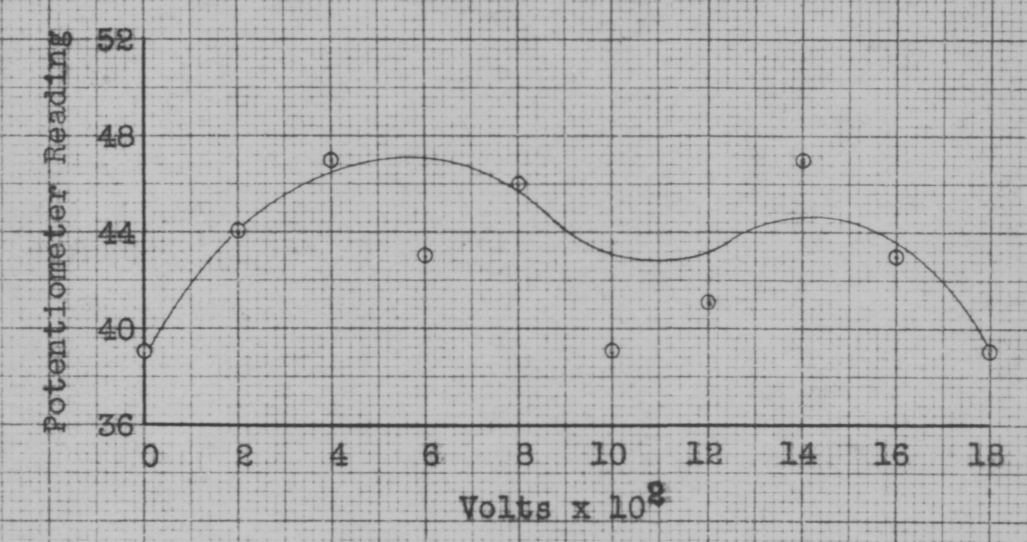
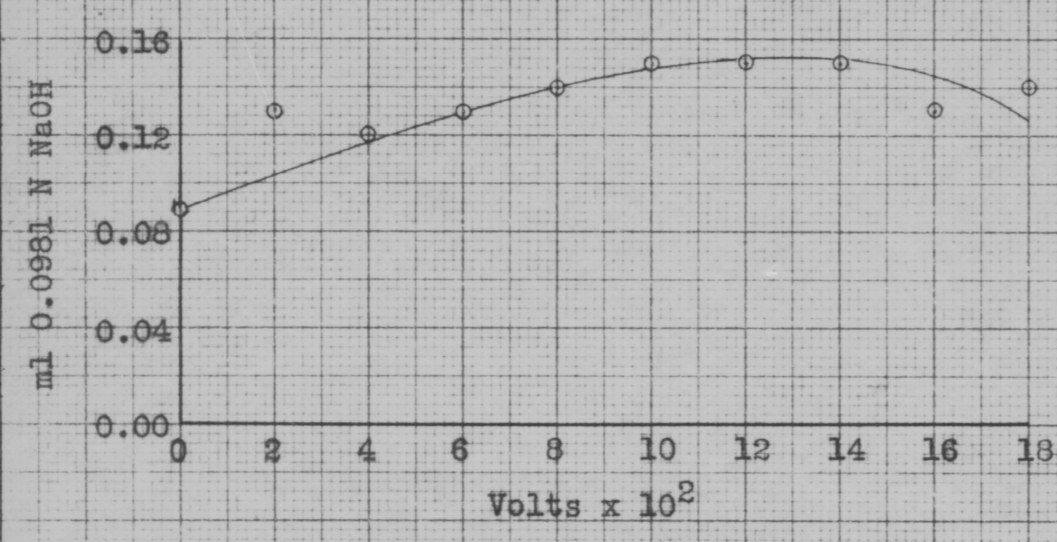
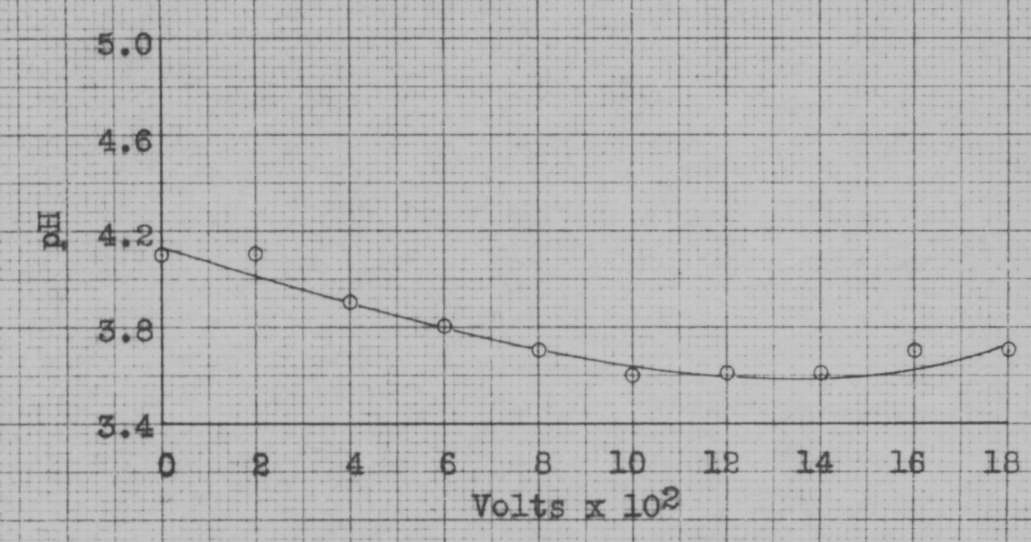
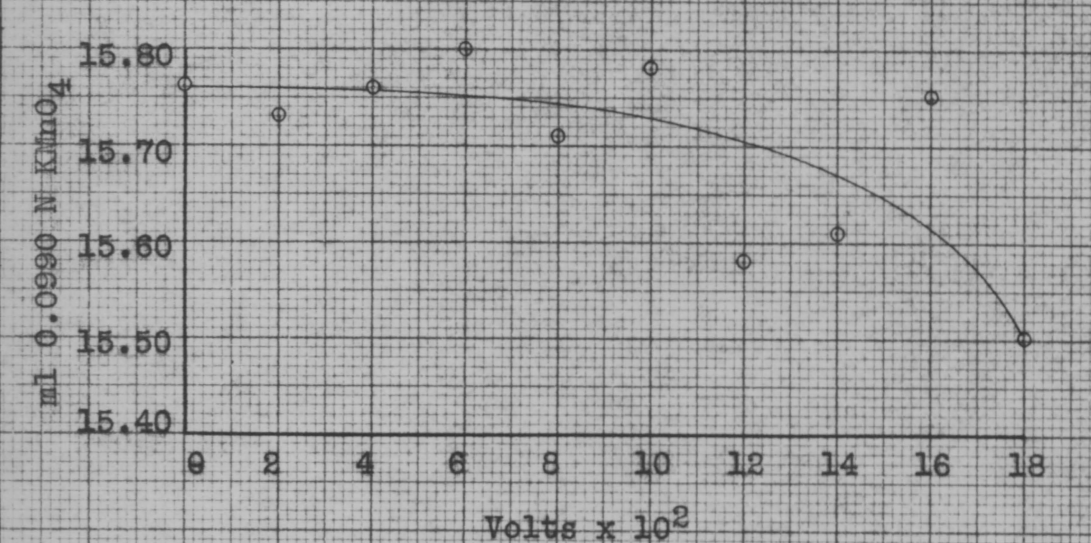
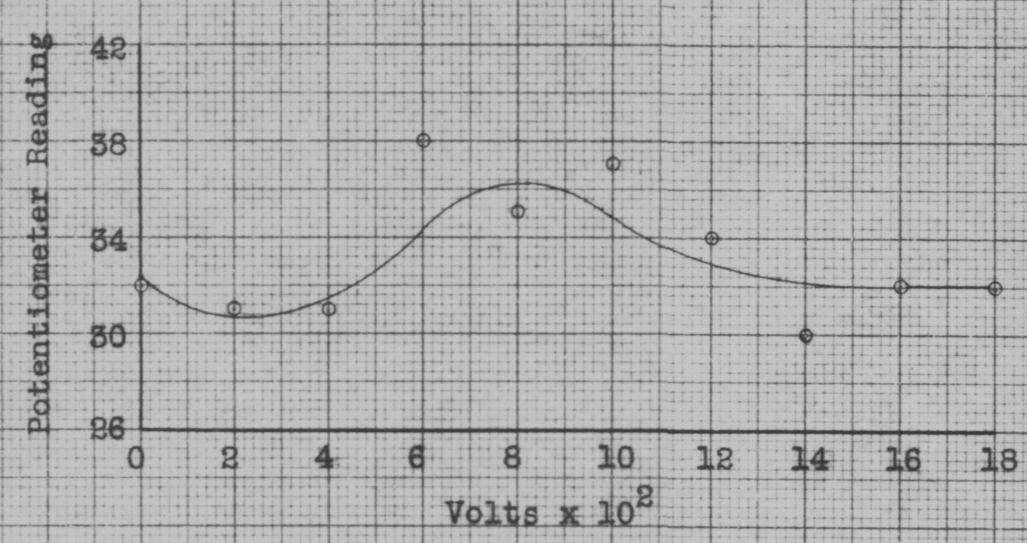
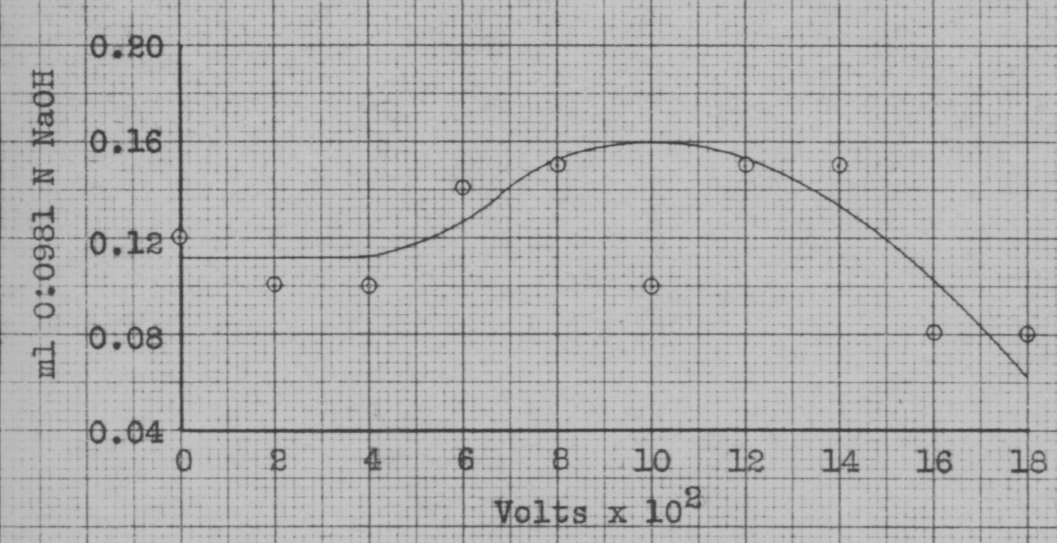
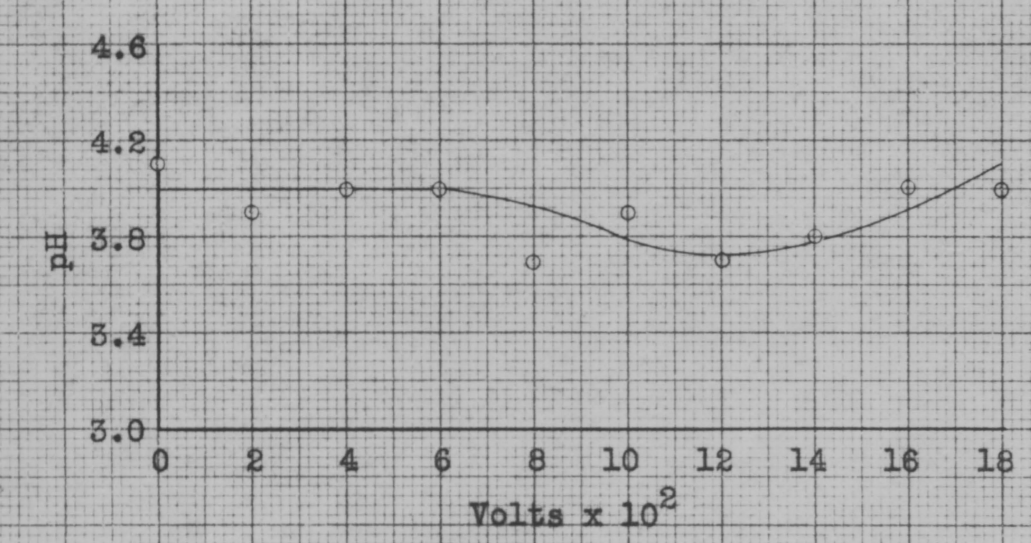
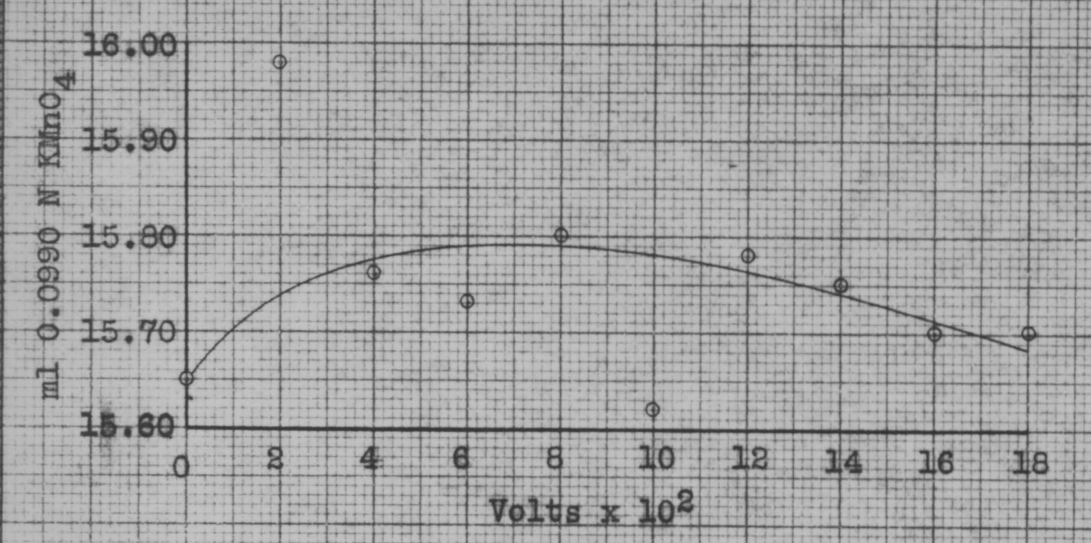
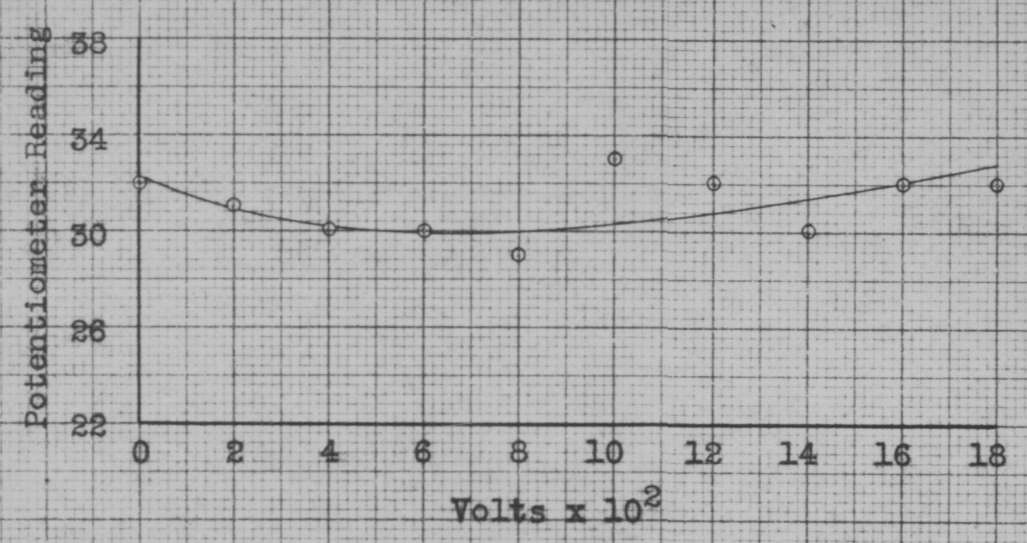
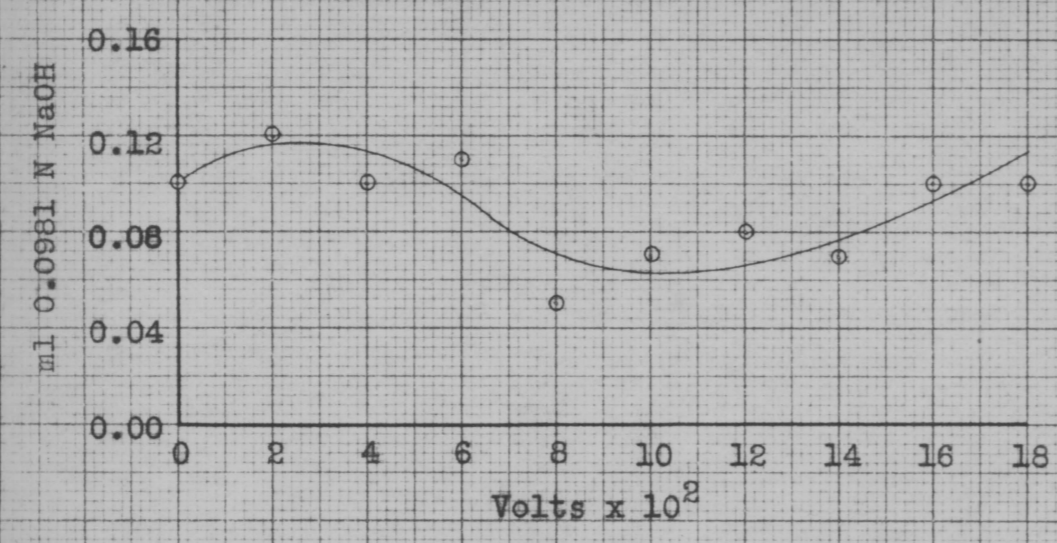
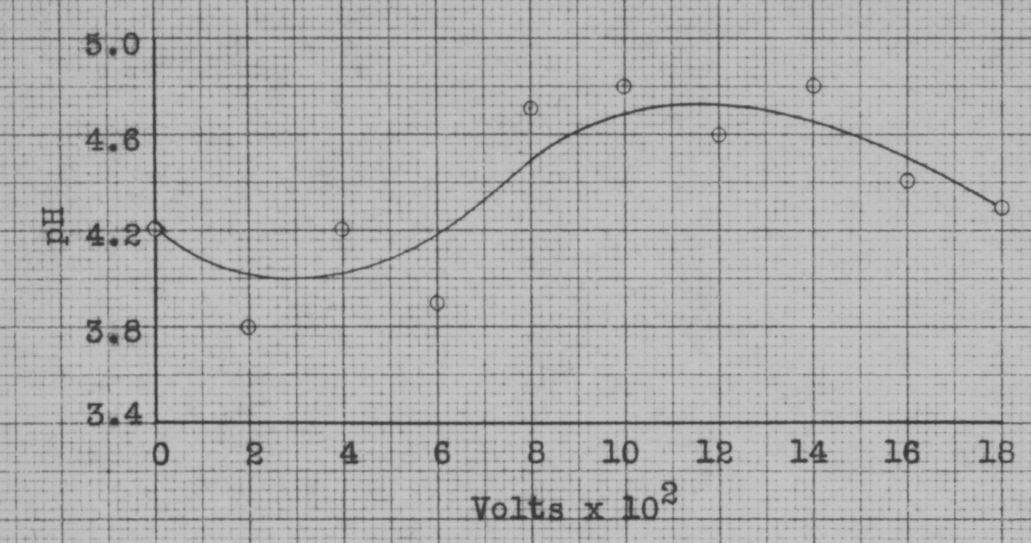
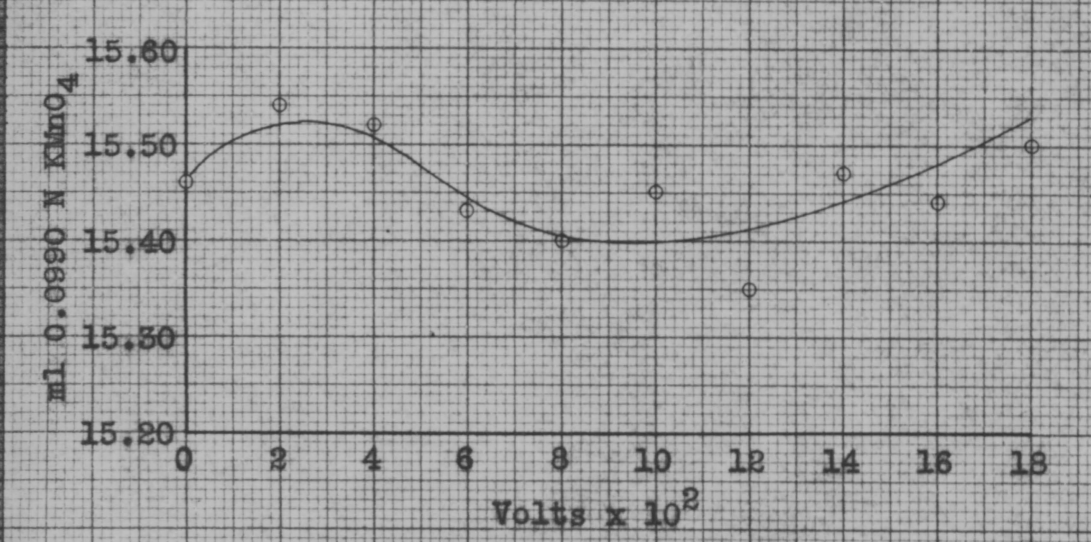
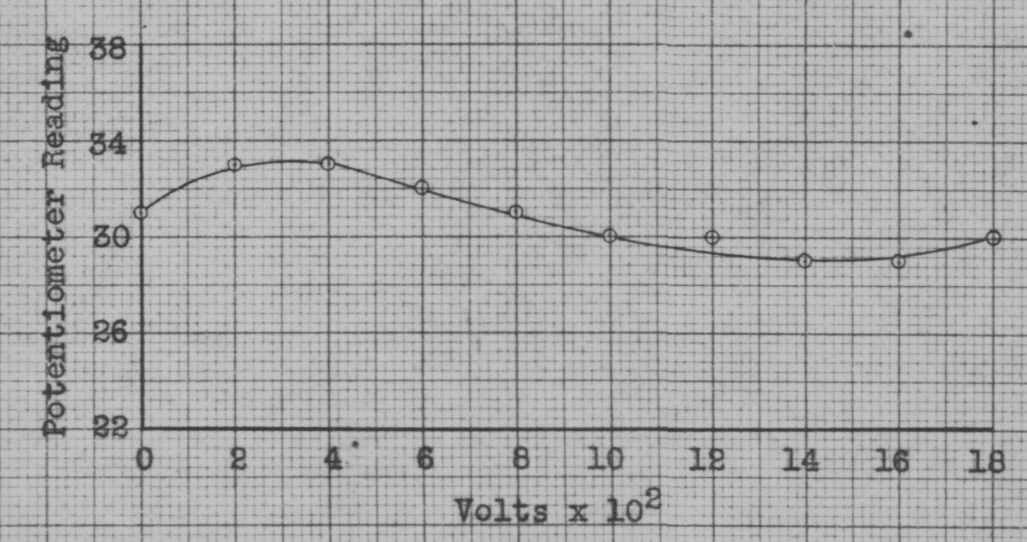
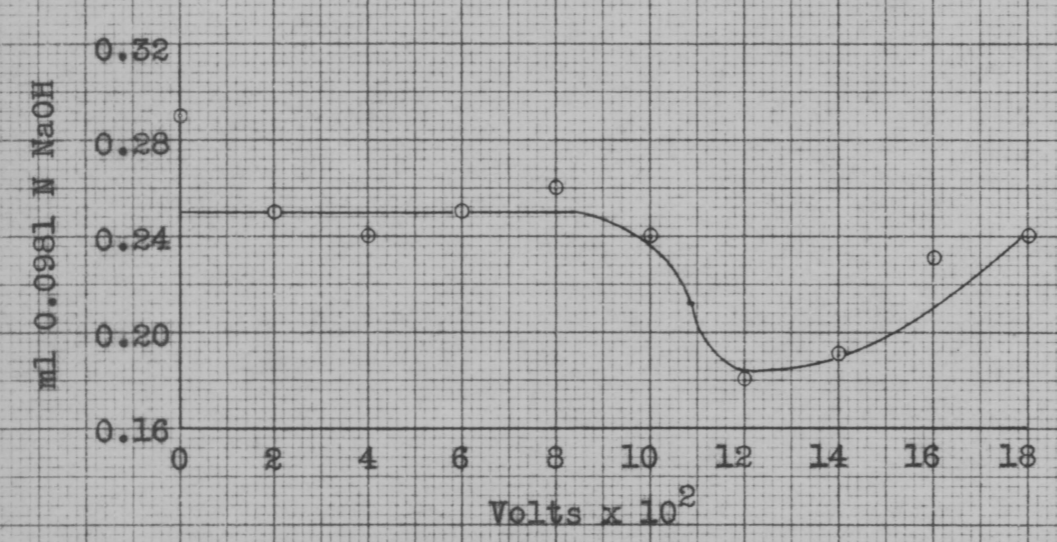
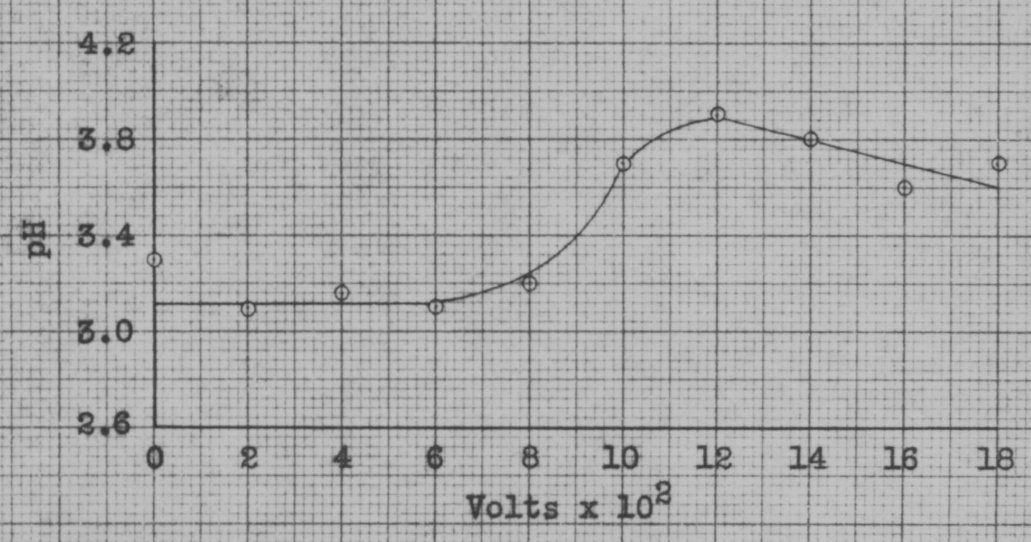
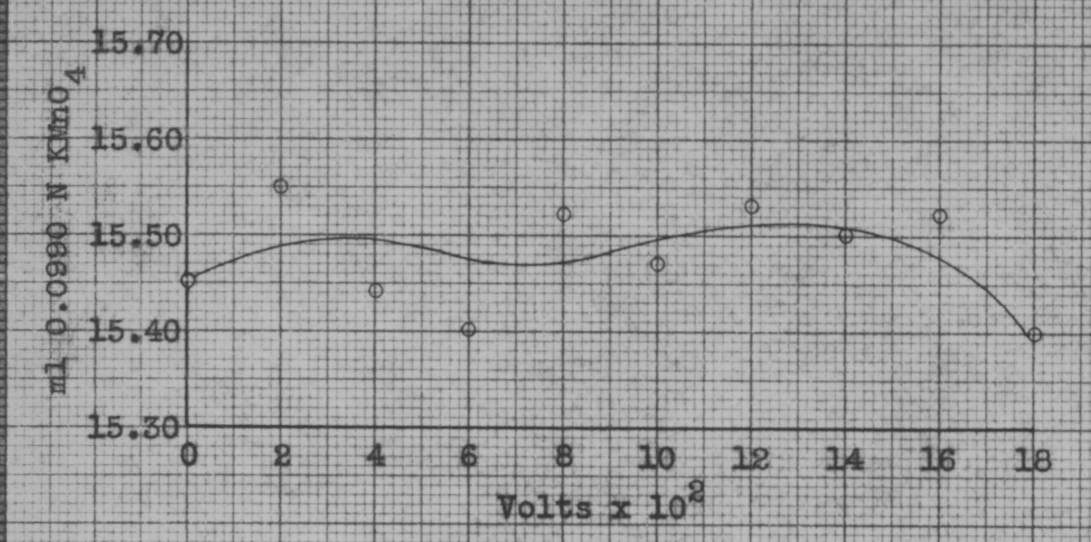
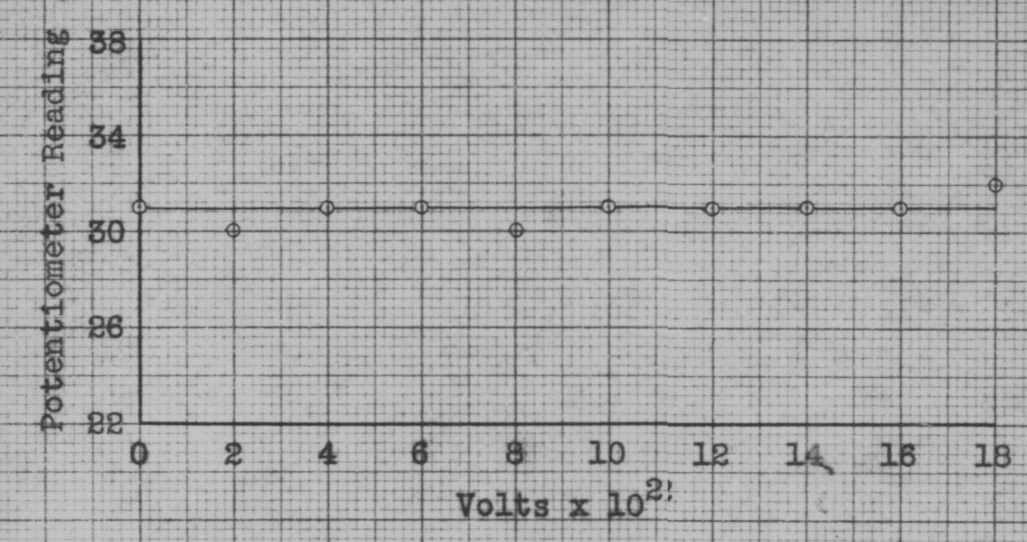
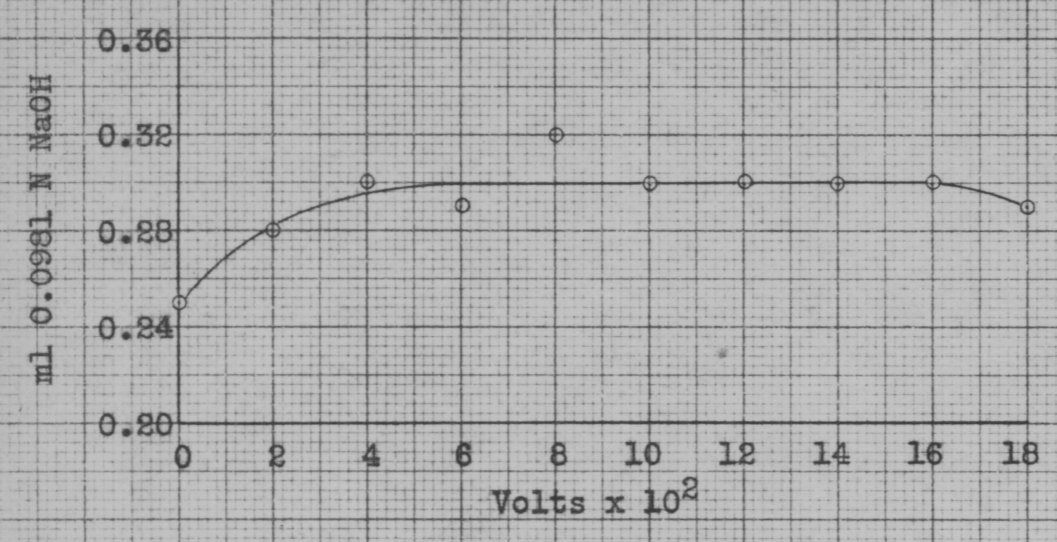
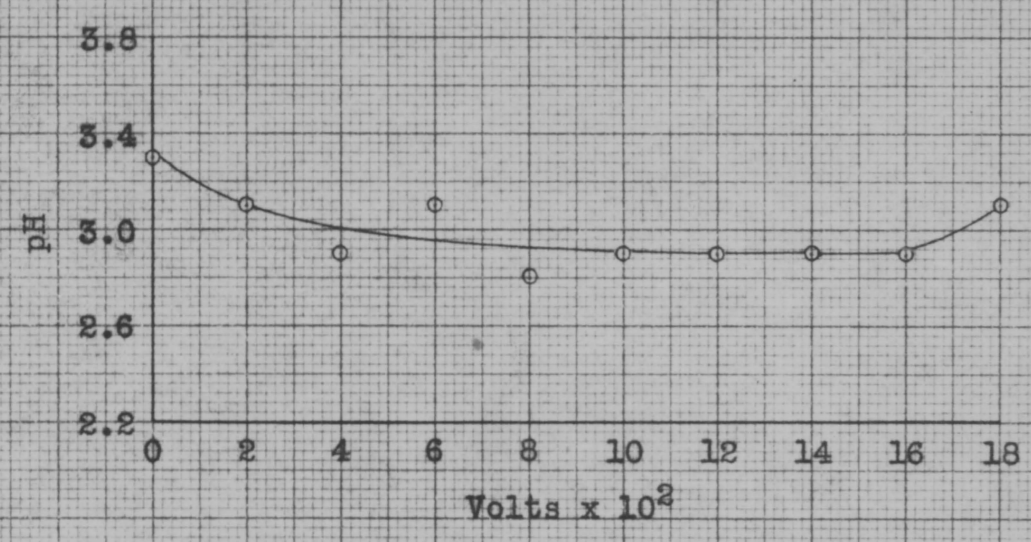


Figure 29

Effect of Ultrasonic Irradiation on the pH of an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture as the Ultrasonic Frequency, Time of Irradiation, and Ultrasonic Intensity Increases

Figure 30

Effect of Ultrasonic Irradiation on the Volume of 0.0981 N Sodium Hydroxide Solution Required to Titrate an Ethyl Alcohol-Hydrogen Peroxide-Water Mixture to a pH of 7 as the

TABLE XIV

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for One Minute at 400 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N $KMnO_4$ ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	30	-0.2	6.0	0.03	12.0	-1	-3.2	0.10	0.64
3	400	52	-0.4	-12.1	0.05	20.0	0	0	-0.01	-0.06
4	600	100	-0.2	-6.0	0.04	16.0	0	0	-0.05	-0.32
5	800	140	-0.5	-12.1	0.07	28.0	-1	-3.2	0.07	0.45
6	1000	170	-0.4	-12.1	0.05	20.0	0	0	0.02	0.12
7	1200	190	-0.4	-12.1	0.05	20.0	-1	-3.2	0.08	0.51
8	1400	240	-0.4	-12.1	0.05	20.0	-1	-3.2	0.08	0.32
9	1600	270	-0.4	-12.1	0.05	20.0	-1	-3.2	0.07	0.45
10	1800	303	-0.2	-6.0	0.04	16.0	0	0	0.05	-0.32
11	2000	360	-0.1	-3.0	0.02	8.0	-1	-3.2	0	0

TABLE XV

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for Twenty Minutes at 400 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N KMnO ₄ ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	30	-0.2	-6.06	-0.04	-13.79	2	6.45	0.08	0.51
3	400	55	-0.15	-4.54	-0.05	-17.24	2	6.45	0.06	0.38
4	600	95	-0.2	-6.06	-0.04	-13.79	1	3.22	-0.03	-0.19
5	800	135	-0.1	-3.03	-0.03	-10.34	0	0	-0.06	-0.38
6	1000	160	0.4	12.12	-0.05	-17.24	-1	-3.22	-0.01	-0.06
7	1200	190	0.6	18.59	-0.11	-37.95	-1	-3.22	-0.11	-0.71
8	1400	240	0.5	15.15	-0.10	-34.50	-2	-6.45	0.01	0.06
9	1600	270	0.2	6.06	-0.06	-20.70	-2	-6.45	-0.02	-0.13
10	1800	310	0.4	12.12	-0.05	-17.24	-1	-3.22	0.04	0.26

TABLE XVI

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for One Minute at 700 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N KMnO ₄ ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	30	-0.4	-9.52	0.02	20.00	-1	-3.12	0.33	2.10
3	400	60	0	0	0	0	-2	-6.25	0.11	0.70
4	600	90	-0.3	-7.14	0.01	10.00	-2	-6.25	0.08	0.51
5	800	130	0.5	11.90	-0.05	-50.00	-3	-9.38	0.15	0.96
6	1000	170	0.6	14.28	-0.03	-30.00	1	3.12	-0.03	-0.19
7	1200	190	0.4	9.52	-0.02	-20.00	0	0	0.13	0.83
8	1400	250	0.6	14.28	-0.03	-30.00	-2	-6.25	0.10	0.64
9	1600	265	0.2	4.77	0	0	0	0	0.05	0.32
10	1800	305	0.1	2.38	0	0	0	0	0.05	0.32

TABLE XVII

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for Twenty Minutes at 700 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N $KMnO_4$ ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	30	-0.2	-4.88	-0.02	-16.68	-1	-3.12	-0.05	-0.19
3	400	70	-0.1	-2.44	-0.02	-16.68	-1	-3.12	0	0
4	600	95	-0.1	-2.44	0.02	16.68	6	18.76	0.04	0.25
5	800	130	-0.4	-9.76	0.05	25.00	3	9.12	-0.05	-0.51
6	1000	175	-0.2	-4.88	-0.02	-16.68	5	15.68	0.02	0.12
7	1200	180	-0.4	-9.76	0.05	25.00	2	6.25	-0.15	-1.14
8	1400	255	-0.3	-7.32	0.05	25.00	-2	-6.25	-0.15	-0.95
9	1600	270	-0.1	-2.44	-0.02	-16.68	0	0	-0.01	-0.06
10	1800	305	-0.1	-2.44	-0.02	-16.68	0	0	-0.25	-1.65

TABLE XVIII

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for One Minute at 1000 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N KMnO ₄ ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	30	0	0	0.04	44.44	5	12.81	-0.06	-0.38
3	400	60	-0.2	-4.88	0.05	55.55	8	20.50	-0.04	-0.26
4	600	95	-0.3	-7.32	0.04	44.44	4	10.25	-0.02	-0.13
5	800	130	-0.4	-9.76	0.05	55.55	7	17.95	-0.08	-0.51
6	1000	165	-0.5	-12.20	0.06	66.66	0	0	0	0
7	1200	195	-0.5	-12.20	0.06	66.66	2	5.12	-0.18	-1.16
8	1400	230	-0.5	-12.20	0.06	66.66	8	20.50	-0.01	-0.06
9	1600	260	-0.4	-9.76	0.04	44.44	4	10.25	-0.09	-0.58
10	1800	320	-0.4	-9.76	0.05	55.55	0	0	-0.11	-0.71

TABLE XIX

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for Twenty Minutes at 1000 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	V	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N KMnO_4 ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	25	-0.1	-2.50	0.02	20.00	2	4.88	0.10	0.64
3	400	65	-0.1	-2.50	0.02	20.00	2	4.88	0.02	0.13
4	600	95	-0.1	-2.50	0.02	20.00	0	0	0.05	0.32
5	800	125	0	0	0.01	10.00	-6	-14.62	0.05	0.32
6	1000	160	0	0	0.02	20.00	-7	-17.08	-0.02	-0.15
7	1200	200	0	0	0.02	20.00	-4	-9.76	-0.05	-0.19
8	1400	225	-0.2	-5.00	0.04	40.00	-5	-7.32	-0.05	-0.22
9	1600	260	-0.2	-5.00	0.04	40.00	-2	-4.88	-0.06	-0.39
10	1800	325	-0.5	-7.50	0.05	50.00	0	0	-0.09	-0.58

TABLE XX

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for One Minute at 1500 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N KMnO ₄ ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	30	0.1	2.56	0	0	2	5.41	-0.02	-0.15
3	400	60	-0.1	-2.56	0.01	9.08	3	8.10	-0.04	-0.25
4	600	100	-0.15	-3.84	0.01	9.08	1	2.70	0.03	0.19
5	800	120	-0.2	-5.12	0.02	18.16	-2	-5.41	0.07	0.45
6	1000	165	-0.15	-3.84	0.01	9.08	-2	-5.41	0.05	0.32
7	1200	200	-0.15	-3.84	0.01	9.08	-2	-5.41	0.05	0.32
8	1400	235	-0.1	-2.56	0	0	-2	-5.41	0.01	0.06
9	1600	250	-0.1	-2.56	0.01	9.08	-2	-5.41	-0.06	-0.38
10	1800	290	-0.1	-2.56	0.01	9.08	-2	-5.41	-0.10	-0.64

TABLE XXI

Composition Changes of Ethyl Alcohol-Hydrogen Peroxide-Water Mixtures
Under Ultrasonic Irradiation for Twenty Minutes at 1500 Kilocycles

Run	Voltage	Amperage	Deviation from Original pH		Deviation from Original Acid Content		Deviation from Original Acetaldehyde Content		Deviation from Original Hydrogen Peroxide Content	
Number	v	ma	Potentiometer Reading	%	0.0981 N NaOH ml	%	Potentiometer Reading	%	0.0990 N KMnO_4 ml	%
1	0	0	0	0	0	0	0	0	0	0
2	200	45	-0.05	-1.28	0.01	10.00	-2	-5.41	0.20	1.28
3	400	70	-0.1	-2.56	0.02	20.00	-3	-8.11	0.15	-0.85
4	600	100	-0.25	-6.42	0.05	30.00	0	0	-0.01	-0.06
5	800	130	-0.3	-7.70	0.04	40.00	3	8.11	-0.05	-0.19
6	1000	160	-0.4	-10.02	0.06	60.00	1	2.71	-0.11	-0.70
7	1200	190	-0.35	-8.97	0.05	50.00	0	0	-0.15	-0.85
8	1400	220	-0.4	-10.02	0.06	60.00	0	0	-0.23	-1.47
9	1600	240	-0.4	-10.02	0.06	60.00	-1	-2.71	-0.15	-0.85
10	1800	260	-0.3	-7.70	0.05	50.00	0	0	-0.05	-0.19

IV. DISCUSSION

General. Most studies in the field of ultrasonics have shown results which are generally relative effects of the action of ultrasonic energy on a substance. These studies are fundamental by virtue of the procedures used and the results reported. In the published literature these procedures are by far more qualitative than quantitative.

In this investigation relative quantitative data have been sought for the effect of ultrasonic irradiation on ethyl alcohol-hydrogen peroxide-water mixtures by using methods of analysis generally known and methods of analysis devised solely for this investigation.

Results Of 400 kc - One Minute Irradiation. By examining the curves in Figures 29a, 30a, 31a, and 32a for the 400 kc - one minute ultrasonic irradiation at different amplitudes on an ethyl alcohol-hydrogen peroxide-water mixture, one may state that the effect of ultrasonic irradiation is to:

a. Decrease the pH of the mixture from 3.3 to about 2.9 as the voltage was increased from 0 to 1600 volts; increase the pH of the mixture from 2.9 to 3.1 as the voltage was increased from 1600 to 1800 volts.

b. Increase the volume from 0.25 to 0.30 ml of 0.0991 N sodium hydroxide solution required to titrate the mixture to a pH of 7 as

the voltage increased from 0 to 1600 volts; decrease the volume of sodium hydroxide required for titration from 0.30 to 0.29 ml as the voltage increased from 1600 to 1800 volts.

c. Cause no apparent effect on the apparent acetaldehyde present in the mixture as the voltage increased from 0 to 1800 volts.

d. Cause an increase in the quantity of hydrogen peroxide when the voltage was increased from 0 to 200 volts. This is substantiated by the volume of 0.0990 N potassium permanganate solution used for titration increasing from 15.45 to 15.55 ml. The quantity of hydrogen peroxide decreased as the voltage was increased from 200 to 600 volts as the volume of potassium permanganate required for titration reduced from 15.55 to 15.40 ml. The quantity of hydrogen peroxide increased as the voltage was increased from 600 to 1200 volts as the volume of potassium permanganate required for titration increased from 15.40 to 15.53 ml. The quantity of hydrogen peroxide decreased as the voltage was increased from 1200 to 1800 volts as the volume of potassium permanganate required for titration decreased from 15.53 to 15.40 ml.

One may state that the pH of the ethyl alcohol-hydrogen peroxide-water mixture was lowered from 3.3 to 2.9 when the voltage was increased from 0 to 1600 volts because some of the acetaldehyde present in the mixture was oxidized to acetic acid. This belief is substantiated by the fact that the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7

increased from 0.25 to 0.30 ml as the voltage was increased from 0 to 1600 volts.

The pH of the mixture increased when the voltage was increased from 1600 to 1800 volts because the hydrogen peroxide probably decomposed and caused the activated oxygen released to oxidize some of the acetic acid to carbon dioxide and water, thus raising the pH of the mixture due to some carbonic acid being formed.

In so far as the curve shown in Figure 31a is concerned, there was no apparent change whatsoever of the acetaldehyde quantity in the ethyl alcohol-hydrogen peroxide-water mixture as the voltage increased. However, this is not believed to be the case. Time and time again, previous investigators have pointed out that water acquires oxidizing properties when irradiated; which is attributable, at least partly, to the hydrogen peroxide formed from dissolved oxygen. Figure 32a shows that the quantity of hydrogen peroxide varies slightly as the amplitude of the 400 kc crystal oscillations were increased. Due to hydrogen peroxide being formed or decomposed, the activated oxygen in both of these processes could oxidize some of the ethyl alcohol to acetaldehyde and at the same time oxidize some of the acetaldehyde to acetic acid.

It was noted that the ethyl alcohol-hydrogen peroxide-water mixture became increasingly turbulent as the voltage was increased. Since the reaction vessel was open to the atmosphere it was entirely possible that air was trapped by this turbulence and carried into

the reaction vessel by the falling mixture. Once this trapped air was brought into the greater mass of the mixture, it was being subjected to ultrasonic forces whose strong mechanical or electrical forces may be great enough to rupture chemical bonds and allow the oxygen in this trapped air to form hydrogen peroxide, and/or oxidize ethyl alcohol to acetaldehyde, and/or oxidize acetaldehyde to acetic acid, and/or oxidize acetic acid to carbon dioxide and water.

It was also noticed that during irradiation small gas bubbles were emitted from the ethyl alcohol-hydrogen peroxide-water mixture. At the lower amplitudes a slight increase of the hydrogen peroxide occurred. These bubbles at the lower amplitudes, before turbulence began, could possibly be formed by a degassing of the mixture and then activated due to cavitation and consequently form hydrogen peroxide. The work of previous investigators support this belief.

By this reasoning the apparent acetaldehyde content remaining constant may be explained as well as the increase in the quantity of hydrogen peroxide and the increase of the pH of the mixture.

Results Of 400 kc - Twenty Minute Irradiation. Curves in Figures 29b, 30b, 31b, and 32b for the 400 kc - twenty minute irradiation at different amplitudes on an ethyl alcohol-hydrogen peroxide-water mixture show that the effect of ultrasonic irradiation is to:

a. Decrease the pH of the mixture from 3.3 to 3.1 when the voltage applied to the quartz crystal was increased from 0 to 600

volts; increase the pH of the mixture from 3.1 to 3.9 when the voltage was increased from 600 to 1200 volts; decrease the pH of the mixture from 3.9 to 3.6 when the voltage was increased from 1200 to 1800 volts.

b. Decrease the volume from 0.29 to 0.25 ml of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 as the voltage increased from 0 to 300 volts; decrease the volume of sodium hydroxide solution required for titration from 0.25 to 0.18 ml as the voltage was increased from 300 to 1200 volts; increase the volume of sodium hydroxide solution required for titration from 0.18 to 0.24 ml as the voltage was increased from 1200 to 1800 volts.

c. Increase the apparent quantity of acetaldehyde in the mixture from 31 to 33 when the voltage was increased from 0 to 400 volts; decrease the apparent acetaldehyde content from 33 to 29 when the voltage was increased from 400 to 1400 volts; increase the apparent acetaldehyde content from 29 to 30 when the voltage was increased from 1400 to 1800 volts.

d. Increase the hydrogen peroxide content of the mixture when the voltage was increased from 0 to 200 volts because the volume of 0.0990 N potassium permanganate solution required for titration increased from 15.46 to 15.54 ml; decrease the hydrogen peroxide content when the voltage was increased from 200 to 1200 volts because the volume of potassium permanganate solution required for titration decreased from 16.54 to 15.35 ml; increase the

hydrogen peroxide content when the voltage was increased from 1200 to 1800 volts because the volume of potassium permanganate required for titration increased from 15.35 to 15.50 ml.

The pH of the ethyl alcohol-hydrogen peroxide-water mixture was lowered when the quantity of the hydrogen peroxide was at a maximum and vice versa. Therefore, this lowering of the pH may be due to acetaldehyde being oxidized to acetic acid. The pH lowering is validated by the volume of sodium hydroxide solution required to titrate the mixture to a pH of 7. In this respect the data for the zero voltage seems too high. No explanation can be given for this element of data except that some experimental error or accidental contamination of the sample being tested was the cause. If this one element of data is thrown out the remaining data are very consistent and in keeping with the other curves.

It is interesting to note that the apparent acetaldehyde content is higher or shows a tendency to increase when the hydrogen peroxide content is at its maximum. This indicates that the hydrogen peroxide is oxidizing some of the ethyl alcohol to acetaldehyde.

When the hydrogen peroxide content is at its lowest, it may be seen in Figures 29b and 31b respectively, that the pH is highest and the apparent acetaldehyde content is nearly that of the blank. An explanation for an increase in the basicity of the mixture is that some of the acetic acid was oxidized to carbon dioxide and water by the decomposing hydrogen peroxide or by the formation of hydrogen peroxide at high voltages where the turbulence was intense.

Results Of 700 kc - One Minute Irradiation. Curves in Figures

29c, 30c, 31c, and 32c show that the effect of 700 kc ultrasonic vibrations for one minute on an ethyl alcohol-hydrogen peroxide-water mixture has the effect of:

a. Decreasing the pH of the mixture from 4.2 to about 3.8 when the voltage was increased from 0 to 400 volts; increasing the pH of the mixture from 3.8 to 4.8 when the voltage was increased from 400 to 1200 volts; decreasing the pH of the mixture from 4.8 to 4.3 when the voltage was increased from 1200 to 1800 volts.

b. Increasing the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 from 0.10 to 0.12 ml when the voltage was increased from 0 to 200 volts; decreasing the volume of sodium hydroxide solution required for titration from 0.12 to 0.06 ml when the voltage was increased from 200 to 1200 volts; increasing the volume of sodium hydroxide solution required for titration from 0.06 to 0.10 ml when the voltage was increased from 1200 to 1800 volts.

c. Decreasing the apparent quantity of acetaldehyde in the solution from 32 to 30 when the voltage was increased from 0 to 600 volts; increasing the apparent quantity of acetaldehyde from 30 to 32 when the voltage was increased from 600 to 1800 volts.

d. Increasing the volume of 0.0980 N potassium permanganate solution required to titrate the hydrogen peroxide content of the mixture from 15.65 to 15.80 ml when the voltage was increased from 0 to 300 volts; and decreasing the volume of potassium permanganate

required for titration from 15.80 to 15.70 ml when the voltage was increased from 800 to 1800 volts.

The pH of the mixture was lowest when the hydrogen peroxide content was highest. In all probability some of the apparent acetaldehyde was oxidized to acetic acid. This belief is further substantiated by the fact that while the hydrogen peroxide content was highest, the apparent acetaldehyde content decreased. Also, the volume of sodium hydroxide solution required to titrate the mixture to a pH of 7 varied accordingly. Certainly this shows that the acid content of the mixture varied as the curve shows for the pH of the mixture.

The increase in hydrogen peroxide content at the lower voltages may be explained by degassing of dissolved oxygen in the hydrogen peroxide. The degassed oxygen could in turn be activated by the ultrasonic energy to produce hydrogen peroxide. At high voltages there would be a tendency for dissociation of the hydrogen peroxide due to turbulence and the high frequency of vibration. This action may well explain the decrease of the hydrogen peroxide content.

The increase in acetaldehyde after 600 volts was applied may be explained by decomposition of hydrogen peroxide to give activated oxygen in the presence of ultrasonic energy, and also the activated oxygen in the air trapped by turbulence. All these factors probably cause some oxidation of the ethyl alcohol in the mixture.

Results Of 700 kc - Twenty Minute Irradiation. Curves in Figures 29d, 30d, 31d, and 32d show that the effect of 700 kc

ultrasonic vibrations for twenty minutes on an ethyl alcohol-hydrogen peroxide-water mixture has the effect to:

a. Decrease the pH of the mixture from 4.2 to 3.7 when the voltage was increased from 0 to 1000 volts and to increase the pH of the mixture from 3.7 to 4.0 when the voltage was increased from 1000 to 1800 volts.

b. Increase the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 from 0.10 to 0.15 ml as the voltage was increased from 0 to 1000 volts and to decrease the volume of sodium hydroxide solution required for titration from 0.15 to 0.08 ml as the voltage was increased from 1000 to 1800 volts.

c. Decrease the apparent acetaldehyde content of the mixture from 32 to 31 as the voltage was increased from 0 to 400 volts; increase the apparent acetaldehyde content from 31 to about 37 as the voltage was increased from 400 to 1000 volts; decrease the apparent acetaldehyde content from about 37 to 32 as the voltage was increased from 1000 to 1800 volts.

d. Decrease the volume from 15.76 to 15.50 ml of 0.0990 N potassium permanganate solution required to titrate the hydrogen peroxide content of the mixture as the voltage was increased from 0 to 1800 volts.

It was believed the pH lowering of the mixture was due to some of the apparent acetaldehyde content of the mixture or some of the ethyl alcohol in the mixture being oxidized to acetic acid. Figure 32d clearly shows that the quantity of hydrogen peroxide in the

mixture was decreased as the voltage was increased. This decrease in hydrogen peroxide content was probably due to the hydrogen peroxide being decomposed by ultrasonic energy and liberating oxygen in the form of gas bubbles which were seen in the mixture being irradiated. These bubbles of oxygen could easily have been activated by the ultrasonic energy and caused oxidation to take place, thereby causing the variations of the pH and the apparent acetaldehyde content of the mixture.

Results Of 1000 kc - One Minute Irradiation. Curves in Figures 29e, 30e, 31e, and 32e show that the effect of 1000 kc ultrasonic vibrations for one minute on an ethyl alcohol-hydrogen peroxide-water mixture has the effect to:

a. Decrease the pH of the mixture from 4.1 to 3.6 as the voltage was increased from 0 to 1400 volts. As the voltage was increased from 1400 to 1800 volts the pH of the mixture increased from 3.6 to 3.7.

b. Increase the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 from 0.10 to 0.15 ml as the voltage was increased from 0 to 1400 volts. As the voltage was increased from 1400 to 1800 volts the volume of sodium hydroxide solution required for titration decreased from 0.15 to 0.14 ml.

c. Increase the apparent acetaldehyde content of the mixture from 39 to about 46 when the voltage was increased from 0 to 600 volts and to decrease the apparent acetaldehyde content of the

mixture from 46 to about 39 when the voltage was increased from 600 to 1800 volts.

d. Increase the volume from 15.50 to 15.43 ml of 0.0990 N potassium permanganate solution required to titrate the hydrogen peroxide in the mixture when the voltage was increased from 0 to 1800 volts.

It is believed the pH lowering of the mixture was due to some of the apparent acetaldehyde content of the mixture or some of the ethyl alcohol being oxidized to acetic acid. Figure 32e clearly shows that the quantity of hydrogen peroxide in the mixture was decreased as the voltage was increased. This decrease in hydrogen peroxide content was probably due to hydrogen peroxide being decomposed by ultrasonic energy and liberating oxygen in the form of bubbles which were seen in the mixture being irradiated. These bubbles of oxygen could easily have been activated by the ultrasonic energy and caused oxidation to take place, thereby giving the variations of the pH and the apparent acetaldehyde content of the mixture.

Results Of 1000 kc - Twenty Minute Irradiation. Curves in Figures 29f, 30f, 31f, and 32f show that the effect of 1000 kc ultrasonic vibrations for twenty minutes on an ethyl alcohol-hydrogen peroxide-water mixture has the effect to:

a. Decrease the pH of the mixture from 4.0 to 3.9 as the voltage was increased from 0 to 600 volts; decrease the pH from 4.0 to

3.7 as the voltage was increased from 1000 to 1800 volts. When the voltage was increased from 600 to 1000 volts the pH of the mixture was increased from 3.7 to 4.0.

b. Increase the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 from 0.10 to 0.12 ml as the voltage was increased from 0 to 800 volts; and from 1000 to 1800 volts the volume of sodium hydroxide solution required for titration was increased from 0.12 to 0.15 ml. As the voltage was increased from 600 to 1000 volts the volume of sodium hydroxide solution required for titration decreased from 0.12 to 0.11 ml.

c. Increase the apparent acetaldehyde content of the mixture from 41 to 45 when the voltage was increased from 0 to 400 volts; increase the apparent acetaldehyde content of the mixture from 34 to 41 when the voltage was increased from 1000 to 1800 volts. When the voltage was increased from 400 to 1000 volts, the apparent acetaldehyde content of the mixture decreased from 45 to 34.

d. Increase the volume of 0.0990 N potassium permanganate solution from 15.50 to 15.65 ml required to titrate the hydrogen peroxide in the mixture as the voltage was increased from 0 to 400 volts. As the voltage was decreased from 400 to 1800 volts, the volume of 0.0990 N potassium permanganate solution required to titrate the mixture was lowered from 15.65 to 15.41 ml.

It was believed the pH lowering of the mixture was due to some of the apparent acetaldehyde content of the mixture or some of the ethyl alcohol in the mixture being oxidized to acetic acid. Figure

30f showing the volume of sodium hydroxide required to titrate the mixture to a pH of 7 substantiates this belief. Also Figure 32f shows the decomposition of the hydrogen peroxide at higher voltages and whose activated oxygen could cause oxidation.

The initial increase in the hydrogen peroxide content of the mixture may have been due to the degassing of the mixture. The oxygen in this degassing could subsequently be activated to produce an increased amount of hydrogen peroxide in the mixture. This action would also account for the increased apparent acetaldehyde content in the mixture at the lower voltages.

Results Of 1500 kc - One Minute Irradiation. Curves in Figures 29g, 30g, 31g, and 32g show the effect of 1500 kc ultrasonic irradiation for one minute on an ethyl alcohol-hydrogen peroxide-water mixture has the effect to:

a. Decrease the pH of the mixture from 3.9 to about 3.8 as the voltage was increased from 0 to 1800 volts.

b. Increase the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 from 0.11 to about 0.12 ml as the voltage was increased from 0 to 1800 volts.

c. Increase the apparent acetaldehyde content of the mixture from 37 to 40 when the voltage was increased from 0 to 400 volts and to decrease the apparent acetaldehyde content from 40 to 35 when the voltage was increased from 400 to 1800 volts.

d. Decrease the volume of 0.0990 N potassium permanganate from 15.60 to 15.56 ml required to titrate the hydrogen peroxide in

the mixture as the voltage was increased from 0 to 400 volts. As the voltage was increased from 400 to 1000 volts the volume of potassium permanganate required for titration increased from 15.66 to 15.67 ml. As the voltage was increased from 1000 to 1300 volts the volume of potassium permanganate required for titration decreased from 15.67 to 15.50 ml.

At the lower voltages it was believed the increase in the apparent acetaldehyde content of the mixture was due to the hydrogen peroxide being decomposed by ultrasonic energy. The oxygen released in this decomposition was probably activated which caused oxidation of some of the apparent acetaldehyde content and/or some of the ethyl alcohol in the mixture. The increase in the volume of sodium hydroxide solution required to titrate the mixture to a pH of 7 is evidence that the acid content of the mixture increased.

At the higher voltages the quantity of hydrogen peroxide diminishes rapidly while the pH of the mixture rises slightly and the apparent acetaldehyde content remains constant. This effect is believed due to some of the acetic acid formed being oxidized to carbon dioxide and water. If this happens it helps to account for the fog produced over the mixture in the reaction tube while being irradiated. It was noticed that the intensity of the fog increased as the voltage was increased. Concurrently, the pH of the mixture also increased as the voltage was increased.

Results Of 1500 kc - Twenty Minute Irradiation. Curves in Figures 29h, 30h, 31h, and 32h show that the effect of 1500 kc

ultrasonic irradiation for twenty minutes on an ethyl alcohol-hydrogen peroxide-water mixture has the effect to:

a. Lower the pH of the mixture from 3.9 to 3.5 as the voltage was increased from 0 to 1400 volts and to increase the pH of the mixture from 3.5 to 3.6 as the voltage was increased from 1400 to 1800 volts.

b. Increase the volume of 0.0981 N sodium hydroxide solution required to titrate the mixture to a pH of 7 from 0.10 to 0.16 ml as the voltage was increased from 0 to 1400 volts and to decrease the volume of sodium hydroxide required for titration from 0.16 to 0.15 ml as the voltage was increased from 1400 to 1800 volts.

c. Decrease the apparent acetaldehyde content of the mixture from 37 to 35 as the voltage was increased from 0 to 200 volts; increase the apparent acetaldehyde content from 35 to 40 as the voltage was increased from 200 to 300 volts; decrease the apparent acetaldehyde content from about 40 to 36 as the voltage was increased from 300 to 1600 volts; and the apparent acetaldehyde content remained constant at about 37 as the voltage was increased from 1600 to 1800 volts.

d. Increase the volume of 0.0990 N potassium permanganate solution from 15.63 to 15.83 ml required to titrate the hydrogen peroxide in the mixture as the voltage was increased from 0 to 200 volts; decrease the volume of potassium permanganate required for titration from 16.33 to 16.48 ml as the voltage was increased from

200 to 1400 volts; increase the volume of potassium permanganate required from 15.45 to 15.60 ml as the voltage was increased from 1400 to 1800 volts.

At the lower voltages it was believed the decrease in the apparent acetaldehyde content and a lowering of the pH was due to oxidation of some of the apparent acetaldehyde to acetic acid. This could easily have taken place because the hydrogen peroxide content was greatest at the lower voltages.

As the voltage was increased to 1400 volts, the hydrogen peroxide content of the mixture decreased which was probably due to decomposition. At the same time the apparent acetaldehyde content of the mixture increased and the pH of the mixture decreased. In all probability the oxygen resulting from the decomposition of the hydrogen peroxide was activated by ultrasonic energy and caused oxidation of some of the ethyl alcohol to acetaldehyde and some of the acetaldehyde to acetic acid. This belief is further substantiated by the fact that the volume of sodium hydroxide required to titrate the mixture to a pH of 7 was increased as the voltage was increased from 0 to 1400 volts.

When the voltage was increased from 1400 to 1800 volts the hydrogen peroxide content of the mixture increased while the pH of the mixture also increased, but the apparent acetaldehyde content of the mixture remained constant. This effect was believed due to the acetic acid being oxidized to carbon dioxide and water. Again, this helps explain the fog formed over the mixture in the reaction

vessel as the voltage was increased. If the acetic acid were oxidized to carbon dioxide and water the acetaldehyde content would have a tendency to remain constant since acetaldehyde was being formed from the ethyl alcohol and also acetaldehyde was being oxidized to give acetic acid.

Recommendations

Analytical Procedures. A more intensive review of the literature should be made in an attempt to locate other methods of analysis that may be applied to this investigation. If further work is done on this subject, some method should be sought to estimate at least the quantity of ethyl alcohol present in the mixture after irradiation; also some method to detect and measure the release of oxygen and carbon dioxide caused respectively by the decomposition of hydrogen peroxide and the oxidation of acetic acid should be sought.

The colorimetric method devised in this investigation for the quantitative determination of the apparent acetaldehyde content should be a subject for individual investigation as well as the published methods for the removal of acetaldehyde from ethyl alcohol.

Mixture Irradiated And Time Of Irradiation: The composition of the mixture subjected to ultrasonic irradiation should be altered by using one-tenth, five-tenths, and twice the mole requirements of hydrogen peroxide required for the given reaction. The time of

ultrasonic irradiation should be varied from a few seconds to one hour on volumes of the mixture varying from 1 to 25 ml.

Reaction Vessel. A reaction vessel and accessories should be designed and constructed of very thin pyrex glass to permit ease in handling, prevent the mixture being thrown out of the vessel by turbulence when irradiated above 1200 volts, allow cooling or heating of the mixture in the reaction vessel, condense vapors that may be evolved during irradiation, and to permit adoption of a means of determining the temperature within the mixture being irradiated.

Miscellaneous. A more compact external cooling unit with optional refrigeration should be provided for the ultrasonicator. A clear plastic or glass plate with holes for the reaction vessel and oil inlet and exit tubes should be placed on top of the transducer glass jar while the ultrasonicator is in use. The clear plate would prevent transformer oil being thrown out of the glass jar when operating above 1200 volts.

Limitations

The results of this investigation were based solely on the following variables with the limitations given:

a. The ultrasonic oscillator was limited to 400, 700, 1000, and 1500 kc quartz crystals. The plate voltage applied to the

quartz crystals could be varied from 0 to 2000 while the plate current increased from 0 to 360 milliamperes as the voltage was increased from 0 to 2000.

b. The impedance matching unit was adjusted so that at a plate voltage of 1250, the plate current was 210 milliamperes; at 1750 volts, the plate current was 300 milliamperes; and at 2000 volts, the plate current was 360 milliamperes.

c. The level of the transducer oil bath above the quartz crystal was maintained at 3 centimeters above the top surface of the coil element porcelain plate of the transducer.

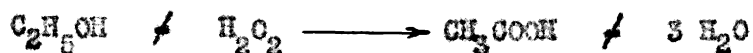
d. The mean temperature of the oil bath was maintained at 68° F by means of an external cooling unit.

e. No attempt was made to control the temperature of the mixture being irradiated other than the cooling caused by the transducer oil bath.

f. The reaction vessel was a flat-bottomed, thin-walled, glass vial one inch in diameter and 3.25 inches in length.

g. With the aid of the human eye for sighting purposes, the reaction vessel was clamped as closely as possible in a vertical position with the geometric axis directly over the intersection of the geometric vertical and horizontal axes of the quartz crystal plate. The bottom of the container was immersed 2 centimeters below the transducer oil level or one centimeter above the top surface of the coil element porcelain plate.

h. The mixture irradiated was made up with a given weight of 95 per-cent ethyl alcohol and the theoretical requirement of 50 per-cent hydrogen peroxide for the reaction,



i. The times of irradiation for each particular frequency and voltage were one minute and 20 minutes respectively.

j. Fifteen milliliters of ethyl alcohol-hydrogen peroxide-water mixture were irradiated.

k. Analytical determinations were made for the pH by means of a Beckman glass electrode pH meter; acid content by titration with 0.0981 N sodium hydroxide; acetaldehyde content by a modified fuchsin-sulfite colorimetric method by means of a Klett-Summerson photoelectric colorimeter; hydrogen peroxide by titration with 0.0990 N potassium permanganate.

l. Chemically pure reagents were used in the investigation.

No claim is made that the methods of procedure or the methods of analysis are infallible. The data recorded may not be considered "absolute" for this reason and also because check determinations were not made.

V. CONCLUSIONS

In the course of this investigation on the effect of ultrasonic irradiation on an ethyl alcohol-hydrogen peroxide-water mixture, the following conclusions are made:

pH

1. 400 kc ultrasonic irradiation for 20 minutes increased the pH of the mixture from 3.1 to 3.9 when the voltage was increased from 600 to 1200.

2. 400 kc ultrasonic irradiation for 20 minutes caused no apparent change of the pH when the voltage was increased from 0 to 600.

3. 400 kc ultrasonic irradiation for 20 minutes decreased the pH of the mixture from 3.9 to 3.6 when the voltage was increased from 1200 to 1800.

4. 400 kc ultrasonic irradiation for one minute decreased the pH of the mixture from 3.3 to 2.9 when the voltage was increased from 0 to 1800.

5. 700 kc ultrasonic irradiation for one minute increased the pH of the mixture from 3.9 to 4.8 when the voltage was increased from 600 to 1200.

6. 700 kc ultrasonic irradiation for 20 minutes caused no apparent change of the pH when the voltage was increased from 0 to 600.

7. 700 kc ultrasonic irradiation for 20 minutes increased the pH of the mixture from 3.7 to 4.0 when the voltage was increased from 800 to 1800.

8. 700 kc ultrasonic irradiation for one minute decreased the pH of the mixture from 4.8 to 4.1 when the voltage was increased from 1200 to 1800.

9. 1000 kc ultrasonic irradiation for one minute decreased the pH of the mixture from 4.1 to 3.6 when the voltage was increased from 0 to 1800.

10. 1000 kc ultrasonic irradiation for 20 minutes decreased the pH of the mixture from 4.0 to 3.7 when the voltage was increased from 0 to 1800.

11. 1500 kc ultrasonic irradiation for one minute decreased the pH of the mixture from 3.9 to 3.8 when the voltage was increased from 0 to 1800.

12. 1500 kc ultrasonic irradiation for 20 minutes decreased the pH of the mixture from 3.9 to 3.5 when the voltage was increased from 0 to 1800.

Klett-Summerson Photoelectric Colorimeter Acetaldehyde Values

The formation of acetaldehyde by the ultrasonic irradiation of ethyl alcohol-hydrogen peroxide-water mixtures can be shown by the relative potentiometer readings on a Klett-Summerson photoelectric colorimeter for a 5-ml blank sample of ethyl alcohol-hydrogen peroxide-water mixture which contained an estimated content of approximately 0.0050 gram of acetaldehyde.

13. The acetaldehyde content of the mixture was not changed at 400 kc ultrasonic irradiation for one minute when the voltage was increased from 0 to 1800.

14. The acetaldehyde content of the mixture was increased from 31 to 33 at 400 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 0 to 400.

15. The acetaldehyde content of the mixture was decreased from 33 to 29 at 400 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 400 to 1800.

16. The acetaldehyde content of the mixture was decreased from 32 to 30 at 700 kc ultrasonic irradiation for one minute when the voltage was increased from 0 to 1800.

17. The acetaldehyde content of the mixture was increased from 31 to 36 at 700 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 400 to 1000.

18. The acetaldehyde content of the mixture was not changed at 700 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 0 to 400 and from 1000 to 1800.

19. The acetaldehyde content of the mixture increased from 39 to 46 at 1000 kc ultrasonic irradiation for one minute when the voltage was increased from 0 to 800.

20. The acetaldehyde content of the mixture decreased from 46 to 39 at 1000 kc ultrasonic irradiation for one minute when the voltage was increased from 800 to 1800.

21. The acetaldehyde content of the mixture decreased from 43 to 34 at 1000 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 0 to 1000.

22. The acetaldehyde content of the mixture increased from 34 to 41 at 1000 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 1000 to 1800.

23. The acetaldehyde content of the mixture increased from 37 to 40 at 1500 kc ultrasonic irradiation for one minute when the voltage was increased from 0 to 400.

24. The acetaldehyde content of the mixture decreased from 40 to 35 at 1500 kc ultrasonic irradiation for one minute when the voltage was increased from 400 to 800.

25. The acetaldehyde content of the mixture was not changed at 1500 kc ultrasonic irradiation for one minute when the voltage was increased from 800 to 1800.

26. The acetaldehyde content of the mixture decreased from 37 to 34 at 1500 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 0 to 400.

27. The acetaldehyde content of the mixture increased from 34 to 38 at 1500 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 400 to 600.

28. The acetaldehyde content of the mixture was not changed at 1500 kc ultrasonic irradiation for 20 minutes when the voltage was increased from 600 to 1800.

General

29. Ethyl alcohol was oxidized to acetic acid by 30-per-cent hydrogen peroxide in only minute quantities when subjected to 400, 700, 1000, and 1500 kc ultrasonic irradiation for one minute and 20 minutes respectively.

VI. SUMMARY

In view of the future of ultrasonics as a tool for the chemical engineering profession and of past events it is not difficult for one to predict that chemical engineers may soon ask what technological advances can be made by means of this relatively new source of energy in industry -- particularly improvements in the process, equipment, and the product.

However, before these questions can be answered, more work will have to be accomplished in the field of ultrasonics to determine quantitative relationships which are presently lacking. Reasoning by analogy does not appear to be the answer in predicting effects caused by ultrasonics.

In this investigation it was desired to determine if hydrogen peroxide oxidized ethyl alcohol to acetaldehyde and subsequently to acetic acid when subjected to ultrasonic irradiation.

The method of procedure and the results of the investigation were based solely on the following variables with the limitations given:

a. The ultrasonic oscillator was limited to 400, 700, 1000, and 1600 kc quartz crystals. The plate voltage applied to the quartz crystals could be varied from 0 to 2000 while the plate current increased from 0 to 360 milliamperes as the voltage was increased from 0 to 2000.

b. The impedance matching unit was adjusted so that at a plate voltage of 1250, the plate current was 210 milliamperes; at 1750 volts, the plate current was 300 milliamperes; and at 2000 volts, the plate current was 360 milliamperes.

c. The level of the transducer oil bath above the quartz crystal was maintained 3 centimeters above the top surface of the coil element porcelain plate of the transducer.

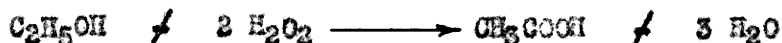
d. The mean temperature of the oil bath was maintained at 68°F by means of an external cooling unit.

e. No attempt was made to control the temperature of the mixture being irradiated other than the cooling caused by the transducer oil bath.

f. The reaction vessel was a flat-bottomed, thin-walled, glass vial one inch in diameter and 3.25 inches in length.

g. With the aid of the human eye for sighting purposes, the reaction vessel was clamped as closely as possible in a vertical position with the geometric axis directly over the intersection of the geometric vertical and horizontal axes of the quartz crystal plate. The bottom of the container was immersed 2 centimeters below the transducer oil level or one centimeter above the top surface of the coil element porcelain plate.

h. The mixture irradiated was made up with a given weight of 95-per-cent ethyl alcohol and the theoretical requirement of 30-per-cent hydrogen peroxide for the reaction,



i. Fifteen milliliters of ethyl alcohol-hydrogen peroxide-water mixture were irradiated.

j. The times of irradiation for each particular frequency and voltage were one minute and 20 minutes respectively.

k. Analytical determinations were made for the pH by means of a Beckman glass electrode pH meter; acid content by titration with 0.0981 N sodium hydroxide; acetaldehyde content by a modified fuchsin-sulfite colorimetric method by means of a Klett-Summerson photoelectric colorimeter; hydrogen peroxide by titration with 0.0990 N potassium permanganate.

The presence of hydrogen peroxide in the mixture irradiated prevented the use of the fuchsin-sulfite colorimetric method as usually given in most standard textbooks for the determination of acetaldehyde. Consequently, the following procedure was used to determine the relative acetaldehyde content of the irradiated mixture:

Five ml of the ethyl alcohol-hydrogen peroxide-water mixture were pipetted into a 50-ml glass-stoppered, volumetric flask, filled with distilled water to the mark, stoppered and then shaken until thoroughly mixed. Five ml of this diluted mixture were pipetted into a 100-ml beaker containing 25 ml of 50-per-cent by volume ethyl alcohol-water mixture at 15°C. Ten ml of fuchsin-sulfite solution at 15°C were immediately added to this mixture and the whole was gently mixed by shaking. A 25 x 150 mm outside diameter lipless pyrex test tube was nearly filled with this mixture and

then stoppered with a number 7 cork. The test tube was kept in a water bath at 30°C for 15 minutes. The relative acetaldehyde content was then determined by using the photoelectric colorimeter.

The results of the investigation show that the effect of ultrasonic irradiation is to oxidise ethyl alcohol to acetaldehyde and subsequently to acetic acid in only minute quantities.

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