INTENSITY DISTRIBUTION IN CYLINDRICAL AND BOWL SHAPED TRANSDUCERS AND SONO-DIALYSIS OF A CAUSTIC SOLUTION

by

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APPROVED:

[Signatures]

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I. INTRODUCTION

In ultrasonic work not much attention has been paid to the measurements of intensity in a sonic field. It is known that ultrasonics produce a host of effects, such as thermal, chemical, physical, medical, biological, colloidal, and electro-mechanical. In the last few years, various attempts have been made to understand these effects. It is thought that cavitation, an intensity dependent phenomenon, is mainly responsible for most of these ultrasonically produced effects. Recently, more and more attention is being paid to the absolute intensity measuring devices at these high frequencies.

At low frequencies the standard equipment is available, such as the sound level meter, for the measurement of absolute intensity. But, at higher frequencies the problem becomes complicated by the diffraction effects on account of the size of the measuring device. A need is indicated, therefore, for the construction of a measuring device which could be used at ultrasonic frequencies.
Ultrasonic transducers have been used in many operations and processes but, generally, their field intensity distributions have not been studied. Usually, it has been assumed that a certain type of intensity distribution would exist as predicted on theoretical grounds.

It was the purpose of this investigation to design and construct an ultrasonic intensity measuring device (the probe), and to evaluate the sonic field distributions in cylindrical (soni-cell) and bowl-shaped transducers; also, to apply the findings from the above mentioned study to the determination of overall mass transfer coefficients in the counter-current dialysis of a caustic solution in the presence and absence of ultrasonics.
II. LITERATURE REVIEW

In the study of the application of ultrasonics to dialysis two major fields, one of diffusion and the other of ultrasonics, are involved. For the purpose of discussion, the literature review has been divided into five sections: (1) diffusion in liquids, (2) dialysis, (3) permeability of membranes, (4) ultrasonics, and (5) application of ultrasonics to diffusional processes.

**Diffusion of Liquids**

Diffusion is defined as a spontaneous transfer of a dissolved substance from one part of a solution to another. It was shown as early as 1850 that the rate of diffusion varies with the nature of the dissolved substance. The quantitative treatment of the diffusion process was reported in literature as early as 1855 with the publication of Fick's law of diffusion.

Fick's Law of Diffusion. It was assumed by Fick that the flow of matter in diffusion follows the same law as the conduction of heat, which had been treated
mathematically by Fourier with the substitution of quantity of the solute for the quantity of heat, and of concentration of solute for temperature. Working on the same analogy, the rate of diffusion, or the amount of substance crossing a given area in an infinitesimally short interval of time, should be proportional to the cross-sectional area and to the concentration gradient. Expressing mathematically

$$dn = -D a (dc/dx)_t dt$$

(1)

where:

$$dn = \text{amount of substance which passes in the time } dt, \text{ mols}$$

$$dc/dx = \text{concentration gradient, mols/cm}^2/cm$$

$$D = \text{diffusion coefficient, cm}^2/\text{sec}$$

$$a = \text{area, cm}^2.$$ 

The negative sign indicates that diffusion takes place from a region of higher concentration to a lower one. It was observed that the value of $D$, for a given solute and solvent, tended to increase somewhat with temperature, and later work has shown that $D$ also tends to increase towards a limiting value as the solution is diluted. It is preferable (72) to refer to $D$ as the
diffusion coefficient rather than as the diffusion constant. Equation (1) is known as Fick's Law.

If area $A$ is kept constant, by the application of the equation of continuity, and the elimination of the dependent variable $A$ of equation (1) the second Fick's Law can be derived\(^{(4)}\). Fick's second law can be expressed mathematically as:

$$\frac{dc}{dt} \left|_x = D \frac{d^2 c}{dx^2} \right. \quad (2)$$

Equation (2) is the most general equation for diffusion in one dimension. It represents a special case of a still more general equation\(^{(75,123)}\) for three-dimensional diffusion processes. The solution of this equation is dependent upon the particular boundary conditions which are imposed.

**Measurement of Diffusion Coefficients.** There are two main procedures which are used to investigate free diffusion occurring across a horizontal boundary in liquid systems\(^{(5)}\). They are, (1) the porous disc method, in which a concentration gradient occurs in the pores of a sintered glass disc, diffusion being followed by removal of samples and estimation of diffusing substance by any analytical means, and
(2) the free boundary method, in which the changes occurring over the free boundary region are investigated optically. Out of these two methods the free boundary method is much more free from theoretical objections, but the porous disc method possesses a great experimental simplicity.

The Porous Disc Method. In one simple form of this method a sintered glass disc with pore size of 5 to 15 microns is mounted at the end of a short glass tube (see Figure 1, page 7). The glass tube is closed by a stop cock. The porous sintered glass disc separates the two homogeneous liquid components of the diffusion system. The heavier component is placed above the lighter one. Diffusion occurs through the pores of the disc on account of the concentration gradient existing there. This concentration gradient may be quite large due to the small pore size. The uniformity in concentration of the two liquids is effected by the slight convection occurring as a result of the density differences set up during diffusion or by some form of stirring the two liquids,
Figure 2, page 9. In this case the stirring is provided by the axial rotation of the cell which contains a glass bead in each compartment for better mixing.

The method consists of placing the disc between known volumes of liquids of known compositions, and by analysis of aliquot samples removed from time to time from both liquids.

The Free Boundary Method. In the free boundary method the solution and solvent (the denser below), initially separated in a vertical tube by some type of barrier, are allowed to come to temperature equilibrium in an accurately controlled thermostat (0.001 to 0.003 °C) provided with good optical observation windows. The barrier is then carefully removed, so forming a sharp boundary between the solvent and solution, which must be kept as free as possible from all forms of disturbance. Vibrational and convectional disturbances particularly must be eliminated, or spuriously high diffusion coefficients would be obtained. Further, any possibility of complication by the diffusion of
Figure 2. Another Form of Porous Disc Apparatus

electrolytes or low molecular weight constituents of the solvent must be removed by a prolonged dialysis of the solution against the solvent before boundary formation.

The formation of a sharp phase boundary is essential for the accuracy of this method of determining diffusion coefficients. Various types (33, 86, 113, 148) of diffusion cells have been reported in the literature for this purpose.

By careful manipulation, sharp boundaries may be formed in all the diffusion cells mentioned above, and the subsequent changes occurring as a result of diffusion may be observed by both absorption and refractive index (5) methods.

**Method of Kegeles and Gosting.** The determination of diffusion coefficient by this method (80) depends on the interference fringe system produced by focussing light through a diffusing boundary. Such an arrangement is said to be accurate and to require very little time. Experimental tests of this method have also been reported (94) in the literature.
Other methods of determination of diffusion coefficients have been reported by Lamm (166), Washburn and Dunning (163), Wall, Greiger, and Childers (162), Wilke (166), Olson and Watson (115), and Gillam (52).

Diffusion and Molecular Size. It has been reported (5) that with increasing molecular weight the diffusion coefficient grows steadily smaller, until for the colloidally disperse materials its value is of the order of 10^{-7} (centimeter)^2 per second, and equalization of concentration after boundary formation occupies a time of at least several days.

It has been found (73) that there exists a linear relation between the diffusion coefficient and the molecular weight of the substance assuming that the diffusing particles are spherical. Such a linear
relation may be obtained by the substitution of appropriate numerical values in the Sutherland-Einstein\(^{(73)}\) equation

\[
D = \frac{RT}{6\pi\eta rN}
\]  

(3)

where:

- \(D\) = diffusion coefficient, \(\text{cm}^2/\text{sec}\)
- \(R\) = gas constant
- \(T\) = absolute temperature, \(^o\text{K}\)
- \(r\) = radius of the particle, \(\text{cm}\)
- \(\eta\) = viscosity, \(\text{centipoise}\)
- \(N\) = Avogadro's Number.

Equation (3) was verified experimentally by Svedberg\(^{(149)}\) for the case of colloidal gold particles of radius 1.3 millimicrons.
The limitations of equation (3) may be shown as follows: If the dissolved substance consists of spherical particles of radius \( r \) and density \( d \), its molecular weight should be

\[
M = \frac{4}{3} \pi r^3 N d \tag{4}
\]

where:

- \( M \) = molecular weight of the substance
- \( r \) = radius of the molecule, \( \text{cm} \)
- \( N \) = Avogadro's Number
- \( d \) = density of the substance, \( \text{gm/cm}^3 \).

If this equation is solved for \( r \), and the resulting expression is substituted in equation (4), it follows that \( d \) should vary inversely as the cube root of \( M \), other factors being constant. For aqueous solutions the viscosity in equation (3) is that of pure water, or one centipoise at 20 °C. For substances of very high molecular weight, namely, the proteins, Svedberg found that the partial specific volume was close to 0.75; hence, density may be taken as 1.33. The
substitution of these figures, with the values of known constants, yields the simple equation

\[ D = 3.21 \times 10^{5/3} / \mathbf{M} \]  

(5)

which should be applicable\(^{(73)}\) to dilute solutions of spherical protein molecules at 20 °C.

**Dialysis**

When colloidal solutions are separated from pure solvent by a porous membrane, which is permeable only to the substances in true solution, the solute in true solution tends to diffuse into the pure solvent through the membrane. In such a case the substances in true solution tend to have the same concentration on both sides of the membrane and as a result diffuse into the pure solvent in order to reach an equilibrium. The process\(^{(93)}\) is called dialysis. If this process is continued for sufficient time with frequent change of the solvent on the other side of the membrane from the sol, practically complete separation of the substances in true solution from those in colloidal solutions can be accomplished. It is said that the sol is now
or dialyzed. A very common and important example is the dialytic purification of biochemical serums or proteins.

The speed of dialysis can be increased by (1) using a large dialyzing surface, (2) stirring, (3) heating, (4) electro-dialysis, (5) increasing size of pores of the dialyzing membrane, and (6) using a constant flowing device.

As has already been said in the section on diffusion, that diffusion and so also dialysis which is a special case of diffusion, follows Fick's equation. In the case of dialysis, diffusion coefficient may be termed as dialysis coefficient.

**Determination of the Dialysis Coefficient.** One simple method has been described recently. The solution to be dialyzed, sodium hydroxide in this case, is separated from the solvent, in this case water, by a permeable cellophane membrane. The experimental arrangement is shown in Figure 3, page 16. Assuming that there is complete mixing in both the solutions and no other concentration gradient exists, except
Figure 3. Simplified Dialysis Cell

at the interface, the above equation can be expressed in the integrated form as follows:\(^{(128)}\):

\[
K = \frac{V_1 V_2}{A (V_1 + V_2) \Delta \theta} \ln \frac{(V_1 + V_2) N_1 - V_1 N_0}{(V_1 + V_2) N_2 - V_1 N_0}
\]  

(6)

where:

- **K** = dialysis constant, cm/min
- **V_1** = liquid in inner container, cm\(^3\)
- **V_2** = liquid in outer container, cm\(^3\)
- **N_1** = solute in \(V_1\) at time \(\theta_1\), gm
- **N_2** = solute in \(V_1\) at time \(\theta_2\), gm
- **N_0** = initial amount of solute in inner container, cm\(^3\)
- **A** = area of the membrane, cm\(^2\).
Application of the Film Concept to Dialysis. As in the case of heat transfer, Fick's equation can be written\(^{(39)}\), for continuous flow in terms of terminal conditions, as

\[ W = U \times A \times \Delta C_{1m} \]  \hspace{1cm} (7)

where:

- \( W \) = weight of material passing through the membrane in unit time, gm/min
- \( U \) = overall dialysis coefficient, \( \frac{\text{gm/min}}{(\text{sq cm})(\text{gm/cc})} \)
- \( A \) = membrane area, sq cm
- \( \Delta C_{1m} \) = logarithmic mean concentration gradient across the membrane
- \( \Delta C_1, \Delta C_2 \) = inlet and outlet concentration differences, respectively.

For batch dialysis a similar equation applies except that \( \Delta C_1 \) and \( \Delta C_2 \) refer to initial and final concentration differences.
Calculation of Dialysis Coefficients. The film concept and that of over-all heat transfer coefficient has been applied to the case of dialysis also. When experimental data are not available the over-all dialysis coefficient may be estimated from the diffusion coefficient, related to the properties of the solution, and from the properties of the membrane being used. Analogous to heat transfer, the resistance to transfer through a membrane is given by a liquid film on each side of the membrane as well as the membrane itself\(^{(39)}\). Thus

\[
\frac{1}{U} = \frac{1}{U_1} + \frac{1}{U_2} \tag{8}
\]

where:

\[
\begin{align*}
\frac{1}{U} & = \text{over-all resistance, min/cm} \\
\frac{1}{U_1} & = \text{combined film resistance, min/cm} \\
\frac{1}{U_2} & = \text{membrane resistance, min/cm}.
\end{align*}
\]
Substituting in equation (8) the diffusion coefficient of the solute and an average value for the combined thickness of the liquid films results

\[ U = \frac{60D}{0.05 + (B/F)} \]  

(9)

where:

- \( U \) = overall dialysis coefficient, \( \text{gm/min} \)/(sq cm)(gm/cc)
- \( D \) = diffusion coefficient, \( \text{cm}^2/\text{sec} \)
- \( B \) = membrane constant
- \( F \) = hindrance factor.

The value of the membrane constant must be determined empirically for each particular membrane from the ratio of the dialysis and diffusion coefficients. Furthermore, the dialysis must be carried out under controlled conditions where the film resistances and hindrance factor are either negligible or calculable. The average membrane pore diameter must also be determined experimentally from the dialysis coefficient of a large molecule of known molecular diameter, the
membrane constant, and the Faxen equation\(^{(9)}\).
The membrane constant is dependent on the degree of swelling of the membrane, which, in turn, is sometimes affected by the solute.

When necessary data are lacking, diffusion coefficients may be estimated from the molecular weight of the solute by various equations given in the literature\(^{(7,121)}\).

**Applications of Dialysis.** Dialysis, which depends on the relative diffusion rates of two solutes, is most efficiently applied to separate low-molecular weight substances in solution from very high-molecular weight substances\(^{(39)}\). Complete separation is possible only if the latter substances are too large to pass through the membrane pores. Dialysis, usually, is a slow process and requires large membrane area if the process has to be carried out in a relatively short time. For example, in the recovery of caustic\(^{(39)}\) one commercial dialyzer of 850 square feet membrane area can handle only 36 gallons per hour of caustic at 90 per cent recovery. Various techniques including ultrafiltration, electro-dialysis, and electro-ultrafiltration, have been developed to shorten the time of dialysis.
Dialysis and applied techniques have been put to use by experimenters for all manner of substances, inorganic as well as organic\(^{(141)}\). In the organic field, the methods have played a great part in the study of bio-colloids such as the proteins, carbohydrates, enzymes, anti-bodies, serums, and horomones. Dialysis has been used by soil chemists to study the organic materials as well as the base-exchange behavior of soils, clays, and minerals. Industrially, also methods of dialysis have considerable importance for the purification of sugar sirups and preparation of medicinals. In Europe, dialysis has been used in purification and dewatering of clays for the clay product industries\(^{(141)}\). Another important industrial application where dialysis finds use is in the separation of spent squeeze liquor from hemicellulose\(^{(98,99,156)}\). Many other applications of dialysis are discussed elsewhere\(^{(144)}\).
Permeability of Membranes

The phenomenon of diffusion through porous membranes finds wide applications in biological and chemical sciences. The subdivision or the enclosure of all living matter by membranes, septa, pellicles, or fluid skins is a fundamental fact of biology. On the other hand, membranes are widely used in the processes of diffusion, dialysis, osmosis, and the allied phenomena. At present, there are large varieties of membranes used in numerous processes.

Semipermeable Membranes. Semipermeable membranes are materials which permit one or more constituents of a solution to pass through, but offer high resistance to the passage of other molecular species which may be present in the solutions. Such membranes are typified by the natural plasma membranes of living cells which play such essential roles in life processes. Artificial semipermeable membranes of numerous types have been known for many years, one example being the semipermeable system formed by a gelatinous precipitate such as copper ferrocyanide. The copper ferrocyanide membrane has been extensively used in studies of the mode of action of such membranes.
Various \((18,19,20,21,76,150,154,161)\) theories have been advanced to explain the permeability behavior of the natural and artificial membranes, but no single theory has been found adequate for all the observed data. There are three main theories which have been advanced to explain the phenomenon of semipermeability. They are: (1) the molecular sieve theory, (2) the solution or phase-distribution theory, and (3) the adsorption theory.

The Molecular Sieve Theory. According to molecular sieve theory, semipermeable membrane possesses pores which allow molecules of small cross-sections to pass through them whereas the large molecules are held back. The inadequacy of this postulation was observed by various investigators \((11,76,150,154,161)\). They found that substances which could not pass through one membrane might pass another with ease, whereas still other solutes to which the first membrane was permeable might be unable to diffuse through the second membrane. For example, rubber membranes were found to be permeable to benzene or pyridine but not to
water in solutions whereas these membranes were impermeable to trichloroacetic acid in aqueous solutions but allowed it to pass when it was dissolved in benzene.

The Solution or Phase Distribution Theory. The solution theory is based on the principle that increased permeability of a given solute is associated with increased solubility of the solute species in the membrane material. Some experiments (64) supported the above theory but many other investigators (18,19,20,21) found the solution theory insufficient in explaining all the observations. It was observed that the osmotic behavior of semipermeable membranes could be simulated by clogging the pores of unglazed porcelain cups with finely divided materials such as barium sulfate, silica, carbon, and metallic silver or gold. Furthermore, the dimensions of the upper limit of pore size for exhibiting these osmotic phenomena were found to be about one micron, which is much larger than the molecular diameter of true crystalloidal solutes.
The Adsorption Theory. The discrepancy in the behavior of clogged porous diaphragms was ascribed to negative adsorption \((100)\) and its significance for the theory of semi-permeable membranes was emphasized \((10)\). The conditions allowing for osmosis with porous or clogged diaphragms have been explained on the basis of negative adsorption. Osmotic phenomena will be observed only when negative adsorption is marked so that the pore walls adsorb practically one component of a solution, and when the pore diameter is sufficiently small so that the film of adsorbate fills the pores completely. However, it is essential that the adsorption of a component be reversible, or the membrane will not allow the diffusing substance to pass.

The molecular sieve membranes have been divided into two categories \((106)\): (1) permeability membranes in which solvents or solutes are more or less soluble, and (2) sieve membranes which act as inert structures with various pore-size classes. Probably, both
categories coexist as has been shown in the preceding discussion.

The sieve membranes are further divided into four classes according to their porosity: (1) open pore membranes such as filter paper retaining only large particles, (2) all filters of less porous materials such as the finest types of filter papers able to retain cells such as blood corpuscles but allowing bacteria and viruses to pass, (3) fine-pored clay, silica, or glass filters retaining bacteria but permeable to colloidal and crystalloidal solutions, and (4) colloid filters of parchment, collodion, or other materials which are permeable only to low-molecular substances.

Various types of membranes have been used in diffusion and dialysis investigations. Some of the more important are cellophane, parchment, collodion, and sintered glass. The comparison of cellophane, "cuprohane," and parchment as dialyzing membranes has been discussed in the literature\(^{29}\). Colorless diffusates have been obtained\(^{122}\) by the dialysis of colored solutions through a semipermeable membrane of film forming water swelling material, for example
hydrophilic cellulose derivatives, denitrated nitrocellulose, casein, or water swelling resins like polyvinyl alcohol, which contain 0.5 to 35.0 per cent by weight of activated carbon.

**Preparation of Dialyzing Membranes.** Dialyzing membranes can be prepared in numerous (18, 30, 31, 36, 37, 38, 95, 96, 97, 112, 145) ways. In many cases their porosity can be controlled. For example (142) the porosity of collodion has been regulated by controlling the degree and rate of drying of the collodion solution after coating. At the proper point of drying which is determined in an empirical manner, the collodion skin is submerged in water in order to leach out the remaining solvents to give an open-pore texture of the sieve-membrane type. However, it is also possible to regulate the porosity of such membranes by introducing into the nitrocellulose solutions higher alcohols such as butanol, or other solvents such as glacial acetic acid.
The term "ultrasonics" is used in acoustics to denote\(^{(15)}\) frequencies which are beyond the limits of hearing of the human ear—that is to say, frequencies of approximately 20,000 cycles per second and greater. By using modern methods of generation it is possible to produce ultrasonic vibrations up to a frequency of about 500 megacycles per second. Expressed in wavelengths this means that ultrasonic waves in air (velocity of sound \(\approx 330 \text{ meters per second}\)) cover a range of 1.6 centimeters to \(0.6 \times 10^{-4}\) centimeters, in liquids (velocity of sound \(\approx 1200 \text{ meters per second}\)) a range of 6 centimeters to \(2.4 \times 10^{-4}\) centimeters, and in solids (velocity of sound \(\approx 4000 \text{ meters per second}\)) a range of 20 centimeters to \(8 \times 10^{-4}\) centimeters\(^{(15)}\). The shortest ultrasonic waves are, therefore, in the order of magnitude of the waves of visible light. Laws of sound valid for the audible range are also true for the ultrasonic range. However, there are phenomena that appear in the ultrasonic range which have not previously been observed in the audible range.
The scope of phenomena produced in an ultrasonic field is extensive (153). In most cases qualitative explanations have been accepted although adequate quantitative data are still lacking. The broad scope of problems, especially in the field of chemical engineering, to which ultrasonics has been applied, fall broadly in the following classes: (1) ultrasonics as an analytical tool, (2) ultrasonics as an engineering tool, (3) ultrasonics in unit operations, and (4) ultrasonics in unit processes. The details of these applications can be looked for elsewhere (153).

Generation of Ultrasonics. In general, there are five essential types of generators for sonic and ultrasonic energy, namely, (1) mechanical, (2) thermal, (3) electrodynamical, (4) magnetostrictive, and (5) piezoelectric generators. Of these, two have shown more promise for industrial applications than the others. The siren type generator, a subdivision of the mechanical type, has been produced commercially in several different sizes and has been used as a means of coagulating dust and fog on an industrial scale employing frequencies at the upper end of
the sonic and lower end of the ultrasonic ranges. The piezoelectric generator has been employed at the highest frequencies and has been used in a variety of ways in liquid and solid systems. It has been employed in submarine communication and detection, testing and gaging of materials, and producing numerous chemical, physical, thermal, and biological effects.

**Piezoelectric Generators.** Piezoelectric generators employ piezoelectric materials. These are the materials which exhibit a reciprocal, nearly linear, relation between alternating mechanical deformation in, and alternating voltage across the specimen. Ultrasonic generators may employ any of the piezoelectric materials such as quartz, barium titanate, EDT (ethyl diamine tartarate), ADP (ammonium dihydrogen phosphate), lithium sulfate, and potassium dihydrogen phosphate. As a matter of fact, each material is better suited for certain applications as compared to other piezoelectric materials. For example, quartz is eminently suited for frequency control, and ADP has been used in Sonar applications. Generally, commercial generators
make use of quartz or barium titanate as the generating material.

**Quartz Transducers.** Although quartz transducers are important in laboratory investigations involving ultrasonic waves they are of limited significance in large scale operations because of the relatively high cost and scarcity of large single crystals of quartz. In addition, there are serious restrictions in the geometric shapes that can be used, and the high alternating current voltages required to drive the quartz transducers often result in an electrical insulation problem.

**Barium Titanate Transducers.** In 1948, the ferro-electric material barium titanate, BaTiO₃, became commercially available in a variety of forms suitable for the generation of ultrasonic waves. This material can be molded into any shape desired and fired in a furnace with suitable metal electrodes on the proper surfaces. Barium titanate can be polarized by simple electrical and thermal means. Despite its polycrystalline nature, the polarized production of
ultrasonic waves is in much the same way as the single crystal of α-quartz. The advantages of the barium titanate ceramic transducers are: (1) the lower cost, (2) the much lower alternating current voltages required to drive them, and (3) the diversified shapes in which they can be produced. With a bowl type transducer, the ultrasonic waves converge at the center of curvature to provide a very high intensity, at the focus. One hundred-fold increments or more in intensity are possible with this focusing action. With a cylindrical transducer a line focus is obtained. The inside and outside surfaces of the cylindrical transducer are covered with conducting silver paint which serves as the electrode. When large barium titanate transducers are desired a mosaic consisting of a number of small hexagonal pieces of ceramic can be cemented together. This technique can be used to line the bottom of a tank or to form a very large concave transducer as shown in Figure 4, page 34. Electrical contact is made to each of the
Figure 4. Mosaic of Hexagonal Elements of Barium Titanate Ceramic

hexagonal elements through wires soldered to the top silver coverings and through the perforated metal plate upon which they are placed. In Table I, page 36, are indicated some of the desirable properties of barium titanate.\(^{(139)}\)

**Effects Produced by Ultrasonics.** Numerous effects\(^{(84,152,153)}\) in solid, liquid, and gaseous systems such as increase in chemical reaction rates, oxidation, electrolytic, polymerization, inversion, crystallization, heating, degassification of liquids and melts, and coagulation effects have been reported by various investigators. These effects can be divided into physical, chemical, thermal, colloidal, biological, and therapeutical effects. Details of these effects can be seen elsewhere.\(^{(16)}\)

The great variety of chemical effects produced by intense ultrasonics has been designated by a new term, sonochemistry\(^{(25,101,107,133,164,165)}\). Among these effects are hydrolysis oxidation, molecular rearrangement, polymerization, depolymerization, and acceleration of chemical reactions. Sonochemistry also includes the development and fixation of photographic films. Though sonochemistry appears
TABLE I

Comparative Chart of Physical Properties of Piezoelectric Crystals

<table>
<thead>
<tr>
<th>Expander Modes</th>
<th>Motion Out Voltage in d $10^{-12}$ m/V</th>
<th>Dielectric Constant $K$</th>
<th>Voltage Out Force in g V·m</th>
<th>Elastic Modulus $Y$ $10^9$ Newton m$^{-1}$</th>
<th>Voltage Out Motion in Yg $10^9$ V·m</th>
<th>Coupling Coefficient $k = \sqrt{\varepsilon_0 \gamma}$</th>
<th>Frequency Constant short-circuited kc.mm</th>
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<td>Rochelle Salt $(34°C)$</td>
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<td>X cut lateral</td>
<td>165</td>
<td>206</td>
<td>.93</td>
<td>19.3</td>
<td>2.9</td>
<td>.54</td>
<td>2100</td>
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<tr>
<td>Y cut lateral</td>
<td>27</td>
<td>9.2</td>
<td>.33</td>
<td>10.7</td>
<td>3.6</td>
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<td>1180</td>
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<td>Lateral</td>
<td>24</td>
<td>15.3</td>
<td>.177</td>
<td>19.3</td>
<td>3.4</td>
<td>.29</td>
<td>1630</td>
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<td>Quartz</td>
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<td>80</td>
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<td>2700</td>
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<td>Lithium Sulfate (LH)</td>
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<td>Parallel</td>
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<td>.033</td>
<td>160</td>
<td>5.3</td>
<td>.10</td>
<td>3600</td>
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<tr>
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<tr>
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<td>.0125</td>
<td>87</td>
<td>1.10</td>
<td>.46</td>
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<td>.0052</td>
<td>87</td>
<td>.45</td>
<td>.19</td>
<td>2090</td>
</tr>
</tbody>
</table>

to have great possibilities it has not yet been established on any large scale; one cause is the relatively high cost of ultrasonic equipment and of power per gram of material converted. Another is that suitable ultrasonic transducers for large volume applications have been developed only recently. For example, tubular transducers of barium titanate excited in their circumferential mode of vibration offer excellent possibilities for continuous flow processing. Such a transducer (156) three inches in diameter and six inches long will absorb up to 500 watts of electrical energy at 22 kilocycles. Any number of such units can be inserted in a pipe line to obtain desired treating capacity; 50 cylinders could absorb 25 kilowatts and process hundreds of gallons per hour in a relatively small space. Recently, a low-cost, high frequency ultrasonic generator has been put in market (156). By this device 10 submersed 400-watt transducers of any type can be energized and copious cavitation obtained throughout a large volume of the solution.

Applications of Ultrasonics. The growth of ultrasonics in the last decade from fundamental
curiosity to extensive applications in medicine, biology, sonar, cleaning, extraction, and other fields indicates the wide interest of researchers in this branch of science. All these advances in its applications have been made possible because of tremendous improvements in the methods of generation of ultrasonics. However, it is still not economical to employ ultrasonics in comparison to other forms of energy. What can be done efficiently, effectively, and economically by mass or macroscopic methods such as mechanical stirring or heating, will be done that way; however, there are many operations that must have microscopic techniques to do the job effectively and efficiently where possibly economics is not the primary consideration. In such applications will lie the greatest importance of ultrasonics as macroscopic methods would not be as efficient.

Ultrasonic applications may be divided broadly in two categories (65), namely: (1) analytical, and (2) processing applications. From the physical point of view these applications may be designated as small-amplitude and large-amplitude applications (62, 101). Flaw detection, underwater
signalling, determination of elastic and molecular properties, viscosimetry are examples of small-amplitude applications, whereas degassing, emulsification, coagulation, surface cleaning, and changing of viscosity are examples of large-amplitude applications.

A few of the applications of high-power ultrasonics are discussed in some detail in the following paragraphs.

Ultrasonic extraction methods have found industrial applications at several large breweries in Germany. Ultrasonics achieves better extraction of the bitter principle from the hops\(^\text{(138)}\); the vegetative bitter is first mechanically torn from the plant umbel and then the small bitter particles are thoroughly dispersed in the beer. The efficiency is increased from 65 to 85 per cent with a saving of the expensive hops to 20 to 25 per cent.

An important application for the ultrasonics is the dispersion of dyes in the rayon and cellulose industry\(^\text{(1,2,3,26)}\). Much better dyeing results have been reported with hard-to-dye fabrics such as orlon using magnetostrictive transducers of about 500 watts acoustic power at 22 and 175 kilocycles per second.
The time to achieve the same color saturation was reduced in some cases to one-sixth.

Efforts have been made to apply ultrasonics in the paint industry. Construction of an ultrasonic pilot plant unit for the dispersion of titanium dioxide in the processing of paint has been reported (101). Possibilities in the lacquer industry (155) where excellent lacquer has been produced by ultrasonically dispersing carbon black to colloidal size, have also been reported.

It is well known that intense ultrasonic waves can emulsify seemingly immiscible liquids like water and mercury (169). Ultrasonic emulsification has not been economically competitive in the past except perhaps for special applications in the pharmaceutical industry and for small quantities. It is reported that 1000 liters of a 20 per cent paraffin emulsion were obtained by recirculation by using the Pohlman ultrasonic whistle. Without ultrasonic processing only a five per cent emulsion could be achieved (101). A high quality shoe polish using ultrasonic processing of the emulsion has been developed in Japan.
The influence of ultrasonics upon flotation ore dressing has been reported in the literature \(118, 119, 147\). Using ultrasonically emulsified frothers in water as flotation reagent, the time of flotation for 89 per cent recovery has been reduced from 15 minutes for nonemulsive reagents to five minutes for ultrasonically processed reagents \(116\).

Ultrasonics has been used \(63\) in the removal of dust particles which stick to the small metal or glass particles by adhesion or because of thin oil or grease film. The materials to be cleaned are immersed in the cleaning bath and irradiated with ultrasonics. It has been found \(105\) that ultrasonics is more economical than hand cleaning. Moreover, better cleaning results when ultrasonics is used. Ultrasonic processing has been found especially useful \(103\) for cleaning precision built work pieces with blind holes and capillary cavities such as injection pumps where as many as 28 tiny cylinders in one block must be cleaned of all traces of lapping compound.

Other important applications of ultrasonics in processing include: (1) rapid degassing of liquids \(103\), in one case at a rate of 2640 gallons
per hour, (2) better vacuum proof joint between ceramic and glass, (3) tinning of aluminum with tin-zinc solder without flux, (4) descaling of metal strips which showed a saving in the pickling acid and also increased the rate of descaling, and (5) improved softening, lining, drenching, tanning, dyeing, and intensification of leather.

These are but a few of the uses to which ultrasonics have been applied. Excellent review articles have been published in the literature. With the improvements in the transducers which can deliver more power, ultrasonics probably would be put to still greater use. For example, it has been recently reported that a five kilowatt generator driven by a 15 horse power motor could energize up to ten submersed 400 watt transducers of any type. Each transformer produced copious cavitation throughout a large volume of the solution. Explosive forces of several hundred atmospheres produced thereby can speed up processing to give more uniform results at lower temperature in many applications. In this way beneficial results can be obtained in polymerization, emulsification, dispersion,
particle size reduction, agglomerization, and agitation of difficult liquids such as molten brine.

Physical Mechanism of Sonic Processes. Discussion here will be concerned only for the study of mechanism when sonic energy is introduced into a liquid system. When the ultrasonic energy is introduced into a liquid system alternate regions of adiabatic compression and rarefaction are set up in the liquid \(^{(66)}\), which move out as a wave from the transducer with a velocity that is characteristic of the elastic properties and the density of the fluid. The wave energy is absorbed in a number of ways \(^{(146)}\). Also, there are several types of steady forces exerted on particles by a sound field \(^{(66)}\). These forces produce a steady drift, rather than oscillation with the sound, and in some cases the particles move in a particular direction with respect to the sound field. Particles suspended in a liquid are acted upon by these forces, and any discontinuity within or at the boundary of a liquid is subject to sonic forces. These forces can produce structural changes in biological tissues, viscoelastic materials, and multiphase chemical systems.
Of particular importance in liquids is the phenomenon of cavitation and the associated formation, oscillation, and collapse of gas or vapor bubbles. Steady forces and cavitation are aspects of large-amplitude sound.

Cavitation. Cavitation is a complex phenomenon (17) which occurs in liquids when the sound pressure amplitude exceeds a critical value and voids are formed in the liquids which subsequently collapse, creating destructive pressure peaks in their immediate neighborhood. Cavitation is essential for most of the processing applications of ultrasonic and bring about definite physical or chemical changes.

If a liquid is exposed to intense ultrasonic vibrations, small bubbles which are formed within the liquid can be observed. Most liquids, unless they are especially treated, contain dissolved or entrained gas. It may be that the gas is present in the form of molecules located at vacant sites of the quasi-crystalline structure of the liquids or it may be contained in invisible bubbles of microscopic dimensions (67). Such bubbles
constitute weak points within the liquid; the tensile strength is determined by the largest bubble present.

It is seen from the literature that little quantitative data has been reported. As a matter of fact, most of the quantitative work in cavitation has been done in the last few years (24, 28, 34, 40, 46, 49, 51, 84, 88, 92, 110, 111, 117, 120, 160, 167) when the importance of cavitation was realized. It can be seen that there must be a maximum tension which a liquid can support without rupture, but it is not clear what bulk properties of the medium determine it. Existing liquid theories which treat pure, homogeneous, ideal liquids consider surface tension as the only parameter which determines the limiting negative pressure the liquid can withstand. Qualitatively, however, air in the liquid, hydrostatic pressure, temperature, and viscosity have been found to have pronounced effects on cavitation threshold pressure (51).

The existing data on cavitation thresholds show a wide disparity between static and acoustic methods of measuring the tensile strength of
liquids. Using water as an example, acoustic data yield cavitation thresholds of the order of one to 10 atmospheres\(^{(23,51)}\). As compared to these values, the values obtained by centrifugal methods for the rupture strengths in water are of the order of 277 atmospheres\(^{(28)}\). Both static and dynamically measured values of cavitation threshold for water fall considerably short of the theoretically predicted values which range from 500 to 10,000 atmospheres.

**The Role of Nuclei and Gas Bubbles.** The impurities and nuclei provide weak points in the structure of a liquid\(^{(51)}\). This fact can be seen from the phenomena of superheating and undercooling. The phenomenon when a "clean" liquid, i.e., one that is free from impurities and gas nuclei, can be heated above its boiling point, is called superheating. Under these conditions external temperature on the liquid can be raised considerably without any transition to vapor phase taking place. But, if a liquid in this state is disturbed, for example, by mechanical shock or an added impurity it will turn explosively to vapor.
Similarly, liquids can be considerably cooled below their melting point without solidification taking place. These observations indicate the effect that impurities can have on the structure of a liquid.

A further proof, that the presence of nuclei is required for cavitation to take place, was provided recently\(^{(46,62)}\). The original idea was that the negative pressure in the sound wave actually tears the liquid apart. However, theoretical considerations made this highly improbable since that would lead to minimum necessary pressures of the order of the "internal pressure"; these internal pressures are usually of the order of several hundred atmospheres, and which are not available in a sound wave. This indicates the requirement for the presence of nuclei. Later, it was shown that undissolved gases were necessary for such nuclei\(^{(62)}\). It was shown that if water is subjected to 1000 atmospheres for 15 minutes and the pressure then removed, no cavitation could be produced for a considerable time. This was explained by the
effective destruction of the centers, the undissolved gas having been forced into solution by the high pressure.

**Stability of Gas Bubbles in the Liquid.** It has been described above that the presence of gas bubbles as nuclei is essential for the production of cavitation. The question arises as to how these small gas bubbles can be stable for any length of time as is required by experiments. This problem has been discussed by various investigators\(^{(23,24,25,68,108)}\) in detail. According to one theory all liquids, even if purified, contain a large number of small dust particles. Their number depends on the heat of wetting, which happens to be particularly high in water. Such dust particles would entrain gas in the form of extremely small bubbles (radius \(10^{-5}\) to \(10^{-4}\) centimeters) which are thus stabilized and kept from going into solution.

The other theory\(^{(46)}\) postulates that gas bubbles which act as cavitation nuclei are stabilized by an organic monomolecular film. This hypothesis has been advanced by some other investigators, also\(^{(46,108)}\).
Gas Bubble Dynamics. A study of the dynamic behavior of bubbles is essential for the understanding of cavitation \(^{(69)}\). Sonic cavitation differs from hydrodynamic cavitation in that it involves an important additional factor of frequency which is absent in the latter. Also associated with this frequency factor is the critical dimension of the bubble at which bubble resonance occurs. The
resonance radius, \( R_0 \), up to the first approximation, is given by the following equation:

\[
R_0 = \frac{\lambda}{2 \pi c} \sqrt{\frac{3 \gamma P_0}{\rho}} \approx (326 \frac{P_0}{\rho})^{1/2}/f \quad (10)
\]

if \( P_0 \gg \frac{2}{R} \) and by:

\[
R_0 = \frac{\lambda}{2 \pi c} \sqrt{\frac{6 \gamma \sigma}{R_0}} \approx (3.9/f)^{2/3} \quad (11)
\]

if \( P_0 \ll \frac{2}{R_0} \)

where:

- \( P_0 \) = total external pressure, atmospheres
- \( R_0 \) = radius of bubble, cm
- \( \gamma \) = ratio of specific heats
- \( f \) = frequency, cycles/sec
- \( \sigma \) = surface tension, dynes/cm
- \( \rho \) = density of the liquid, gm/cm\(^3\)
- \( \zeta \) = density of the liquid, gm/cm\(^3\)
- \( c \) = velocity of sound in liquid, cm/sec
- \( \lambda \) = wave-length of sound, cm.
It is reported in the literature\textsuperscript{(69,110)} that only the bubbles which are smaller than resonant size are capable of rupture and subsequent collapse before the end of the pressure cycle. Experimental evidence also indicates that smallest stable bubbles have radii of the order of $5 \times 10^{-7}$ (0.5 micron).

**Behavior of the Bubble During Collapse.** The higher the ratio of the maximum bubble radius $R_m$ to the initial radius $R_0$ the more violent is the collapse\textsuperscript{(69)}. For a given initial radius $R_0$ the ratio $R_m/R_0$ increases with the sound-pressure amplitude at constant frequency, and decreases with increasing frequency at constant sound pressure. If both sound pressure and frequency are kept constant the ratio $R_m/R_0$ increases if the initial bubble radius $R_0$ is reduced.

During collapse, the walls of the bubble rush inward until the cushioning action of the gas within the bubble stops the radial motion. At the end of the collapse the contents of the bubble are highly compressed and high instantaneous temperatures\textsuperscript{(69,110)} may occur within the bubble, depending on the degree to which adiabatic conditions prevail. These high
local temperatures, which are confined to the gas and vapor content of the bubble, may lead to ionization effects as evidenced by luminescence and formation of OH radicals and peroxide. This mechanism is believed to be responsible for some of the chemical and biological effects that have been observed in the presence of cavitation.

In the liquid itself, temperature effects will be negligible, the main effect being caused by the shock waves that emanate from the cavitation centers. The peak pressures of such shock waves have been measured\(^{(69)}\) with small crystal probes. At 10 kilocycles per second, with an initial bubble radius of about 100 microns and a sound-pressure amplitude of one atmosphere, the shock waves have a peak pressure of 200 to 500 atmospheres at a distance 0.1 centimeter from the bubble center.

**Frequency Dependence of Ultrasonic Cavitation.**

On page 53 is presented a table which gives the published data on certain phenomena and the frequencies at which they occurred\(^{(49)}\). It is noticed that while there is extensive destructive action in the range from a few kilocycles up to about one
<table>
<thead>
<tr>
<th>Frequency of sound field</th>
<th>Phenomenon</th>
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<tbody>
<tr>
<td>400 to 1000 kc</td>
<td>Weak degassing and emulsification</td>
</tr>
<tr>
<td>1-100 kc</td>
<td>Dispersal of metals after Claus</td>
</tr>
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<td>1-7 ke</td>
<td>Effects to colloidal chemistry</td>
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</tr>
<tr>
<td>10-20 ke</td>
<td>Depolymerization</td>
</tr>
<tr>
<td>20-30 ke</td>
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<td>Luminescence of cavitating liquids</td>
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<tr>
<td>1000-2000 ke</td>
<td>Good degassing, cavitation, cavitation and emulsification</td>
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<tr>
<td>320000-325000 ke</td>
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</tr>
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</table>

megacycle, no effects which could be attributed to cavitation have been reported above 2.5 megacycles. It may therefore be inferred\(^{(49)}\) that at the intensities ordinarily reached with present ultrasonic generators no pronounced cavitation occurs at the higher frequencies.

Theoretical considerations\(^{(50)}\) indicate that the optimum frequency for applications of ultrasonics utilizing cavitation effects lies below two megacycles per second and most likely below one megacycle per second at the intensities reached with ordinary transducers.

It has been calculated\(^{(164)}\) that when a sound wave of one megacycle frequency and of high intensity (10 watts per centimeter square) passes through water, it produces, in water molecules, an acceleration of about 250,000 times greater than the acceleration due to gravity. The maximum instantaneous velocity is 40 centimeters per second, and the pressure at a given point in the water changes from +5 atmospheres to -5 atmospheres, one million times each second. Obstacles in the path of the wave experience a
repulsive force along the direction of propagation, due to the radiation pressure of roughly one gram per square centimeter.

**Application of Ultrasonics to Diffusional Processes**

The effect of ultrasonics on diffusional processes is not a much studied field. From the literature it appears that not much work has been done in this direction. Especially, the work on the applications of ultrasonics to dialysis is very little. This section has been divided into two parts, namely, (1) ultrasonics and diffusion, and (2) ultrasonics and dialysis.

**Ultrasonics and Diffusion.** It appears from the literature that the study in the field of ultrasonics and diffusion was started only recently (1, 2, 3, 8, 12, 13, 14, 41, 45, 47, 48, 56, 77, 85, 89, 90, 124, 125, 126, 130, 131, 134, 135, 168). Most of the work has been in the field of medicine, biology, dyeing of fibers, tanning of leather, and sugar extraction from beet roots.

In one of the studies of the effects of ultrasonics on dyeing of fibers it was reported (27) that
equalization of dye bath concentration took place through intense agitation produced by ultrasonics. Also, improved dye dispersion was obtained. It was found that sonic waves of 50 kilocycles per second had little effect on poor dye penetration and crocking in hard fabrics like cotton, poplin, and linen, but considerably deepened the shade in viscose, rayon, cotton, linen, and nylon, without changing characteristics of dye. Sound waves of three kilocycles per second had similar effects but in slightly greater degree. High frequency waves, of the order of 22 kilocycles and 175 kilocycles per second were more effective for dyeing silk, wool, and nylon. With ultrasonics, viscose rayon could be dyed even without preliminary scouring, and yielded good penetration in hard weaves. The dyeing time was reduced to 1/4 or 1/6 of the normal. However, in another investigation it was shown that the rate of dye uptake in the frequency range of 22 to 175 kilocycles per second is practically independent of the frequency, but was accelerated by increasing intensity\(^{(124)}\).

Though these experiments indicate that dyeing rate is improved and better results are obtained in
the presence of ultrasonics no concrete explanation has been advanced as regards to its mechanism. The only hypothesis given seems to be that ultrasonics apparently increases the diffusion rate of the dye in the textile fiber. This view seems to be shared by some other workers\(^{6,13}\) also.

**Ultrasonics and Dialysis.** The literature in the field of application of ultrasonics to dialysis, or diffusion through membranes, is still scanty. To the author's knowledge not much work has been done in this direction.

In a recent study\(^{128}\) of the effect of sonic energy on the dialysis of sodium hydroxide through cellophane membrane, it was shown that the effect was to increase the dialysis constant with ultrasonics then without it. In this investigation the frequency range studied was from 10.9 to 32.7 kilocycles per second and power input from zero to 70 watts. The ratio of the mass transfer coefficient for the transport of alkali through the membrane with sound to that without sound was taken as a measure of the effect of sound energy. These data on the variation of dialysis constant with frequency and
intensity is shown in Table III, page 59. These data are also shown in the form of a graph in Figure 5, page 60.

It has been reported(13) that diffusion of a five per cent sodium chloride solution through a cellophane membrane was increased by a factor of about two under the influence of ultrasonics. It was also found that exposure to ultrasonics increased the diffusion whether the direction of sound was in the direction of diffusion or counter to it.

Dialysis through frog skin as a membrane has been studied by Lehmann and Kruse(9). It was observed that pulsed or continuous ultrasonic energy of therapeutic intensities had the same effect on transport of ions through frog skin in Ringer solution, on permeability, and on diffusion processes. This effect of the increased diffusion was explained on account of the increase in temperature caused by the absorption of ultrasound at the membrane.

Whereas, the above authors point out that increased diffusion is due to increased temperature caused by the absorption of ultrasound at the
### TABLE III

**Variation of Dialysis Constant with Frequency and Intensity**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Frequency Cycles/Sec</th>
<th>Power Input Watts</th>
<th>Dialysis Constant K Cm/Min</th>
<th>% Increase of Base</th>
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<tr>
<td>2</td>
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<td>0</td>
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</tr>
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<td>40</td>
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<td>6</td>
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<td>65</td>
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</tr>
<tr>
<td>31</td>
<td>32,700</td>
<td>50</td>
<td>0.0372</td>
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<tr>
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<td>32,700</td>
<td>70</td>
<td>0.0380</td>
<td>35.5</td>
</tr>
</tbody>
</table>

Figure 5. Variation of Dialysis Coefficient with Power Input at Various Frequencies

membrane, some other investigators have found, experi-
mentally and theoretically, that ultrasonics would
enhance the diffusion process \((6,13)\).
III. EXPERIMENTAL

The experimental section includes the purpose of investigation, plan of experimentation, materials used in the investigation, design and construction of apparatus, method of procedure, data and results obtained, and a sample of the calculations.

**Purpose of Investigation**

The purpose of this investigation was to design and construct an ultrasonic probe for intensity determinations, its evaluation in cylindrical and bowl shaped barium titanate transducers, and also to determine the mass transfer coefficients in continuous countercurrent dialysis of sodium hydroxide solution in the presence and absence of ultrasonics using cellophane as the permeable membrane. In this investigation, study of dialysis with ultrasonics has been designated as "sono-dialysis."
Plan of Experimentation

The plan of experimentation consists of the following: (1) literature review, (2) design, construction, and evaluation of the ultrasonic probe, (3) selection of a solute for sono-dialysis, (4) selection of the membrane, (5) design and construction of the pilot plant, (6) dialyzing cell, and (7) study of the effects of ultrasonics on the mass transfer through a cellophane membrane.

Literature Survey. A search of the literature was made to study the previous work done in the fields of ultrasonic intensity determinations, diffusion, properties of permeable membranes, dialysis, and the effect of ultrasonics on diffusional processes. The two major fields involved were diffusion and ultrasonics.

Design, Construction, and Evaluation of Ultrasonic Probe. An electro-acoustical probe, using a very small cylindrical barium titanate element one-sixteenth inch in length and one-sixteenth inch in diameter as a detector-convertor, was designed and constructed. It was evaluated in a RICH-ROTH soni-cell (a cylindrical transducer) and BRUSH HYPERSONIC bowl shaped transducer.
Selection of Solute. The selection of the solute was influenced by the following considerations: (1) water soluble, as water was used as solvent, (2) low molecular weight, so that it will diffuse through the cellophane membrane, (3) non-corrosivity with copper at room temperature (25 °C) and at the concentration studied, (4) ease and accuracy of analysis, and (5) availability of previous data on its dialysis with water.

Selection of Permeable Membrane. The selection of the membrane was based on the following considerations: (1) average pore size of 25 to 50 Ångstroms, (2) wall thickness; should be thin enough to allow easy passage of solute and ultrasonics, (3) mechanical strength, should be of sufficient strength to stand careful handling in the laboratory in contact with water and dilute caustic solutions, (4) cylindrical shape; to conform to the cylindrical transducer, (5) diameter about one to one and three-fourths of an inch to fit in the transducer, and (6) availability in the market.

Design and Construction of the Pilot Plant. The major pieces of the equipment which were designed and
constructed were: (1) electrical and hydraulic panels, (2) the angle iron supports for the solvent and solution tanks, (3) dialyzing cell, (4) arrangement for the measurement of radio frequency voltage and current input to the transducer (or soni-cell), and (5) arrangement to obtain dry and carbon dioxide-free air from atmosphere.

Dialyzing Cell. The design and construction of the dialyzing cell was a major part of this investigation. The main considerations were the diameter of the membrane and the technique of mounting the membrane so that a smooth, cylindrical surface without any crimps is obtained.

Effect of Ultrasonics on Sono-dialysis. Not much work has been reported in the literature about the effect of ultrasonics on diffusion through permeable membranes. Frequency and intensity are considered to be major variables in the study of ultrasonic effects. Studies of sono-dialysis could not be made at various frequencies on account of certain limitations of the ultrasonic generator. However, it appears from the literature that insonation should increase the mass transfer coefficient through the cellophane membrane.
Materials

The source and description of all materials used in this investigation are listed below. All details relative to identification that will aid in the duplication of the materials have been listed. Construction materials and items of apparatus employed in the design and construction phase of the investigation are shown in Table IV, page 67.

**Acid, Hydrochloric.** CP; lot No E111005. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in titrimetric procedures for the analysis of raffinate and extract.

**Ascarite.** Size 8-20 mesh; lot No 2709. Obtained from Arthur H. Thomas Company, Philadelphia, Pa. Used as carbon dioxide absorbent to obtain carbon dioxide free air.

**Barium Titanate Transducer.** Cylindrical transducer, 1/16-inch O. D. and 1/16-inch long. Obtained from Brush Electronics Co., Cleveland, Ohio. Used as detector-convertor in the ultrasonic probe.

**Cement, Duco.** Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used as cement in the
TABLE IV

**Construction Materials and Items of Apparatus Employed in the Design and Construction of Sono-Dialysis Equipment**

(See Pocket in Appendix)
construction of ultrasonic probe and in the arrangement for holding water over barium titanate bowl shaped transducer.


**Drierite.** Size 8 mesh. Obtained from W. A. Hammond Drierite Co., Xenia, Ohio. Used as absorbent for moisture to obtain moisture-free air.

**Electricity.** Alternating current, 115 volts, 60 cycle. Obtained from VPI Power House. Used as source of energy for operation of electrical equipment.

**Methyl Orange, Powder.** Lot No 52946. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as indicator in titrations.

**Sodium Hydroxide.** Pellets, 'Baker Analyzed' reagent; lot No 9317. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as solute in dialysis.

Tubing, Capillary. Pyrex, outside diameter 5 to 6 mm; bore approximately 1/4 to 3/4 mm; catalog No I1-367. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in metering sodium hydroxide solution and water.

Tubing, Cellophane. Visking seamless cellulose tubing, inflated diameter 36/32 inch. Obtained from The Visking Corp., Chicago, Ill. Used in the construction of dialyzing cell.


Tubing, Glass. Corning brand, alkali resistant, 5/16 inch outside diameter. Obtained from Phipps and Bird, Inc., Richmond, Va. Used in the construction of dialyzing cell and also for inlet and outlet for water in the soni-cell.

Water, Distilled. Obtained from Barnstead still in VPI Chemical Engineering Department. Used as solvent in the dialysis studies.
Water, Tap. Obtained from VPI water mains. Used as cooling medium for transducer (soni-cell) and various other cleaning and washing purposes.

**Equipment**

This section consists of the detailed description of identifying information for various pieces of equipment and assemblies of the dialyzing cell and barium titanate probe for intensity measurements, as both of these pieces of equipment were specially designed for this investigation.

**Ammeter, Radio Frequency.** Serial No 1160336 (W) meter, type RT-37, 4-1/2 inch size, range 0-5 amperes. Obtained from Westinghouse Electric Supply Co., Roanoke, Va. Used to measure the current input to the soni-cell.

**Voltmeter, Vacuum Tube.** Hewlett Packard, model 400D vacuum tube voltmeter, cabinet mount, serial No 5463. Obtained from Hewlett Packard Co., Palo Alto, Calif. Used to measure voltages generated in the measurements of intensity by probe, and also to measure radio frequency voltage input to the soni-cell.
Ultrasonic Equipment. The ultrasonic equipment used in this investigation is discussed under the following headings: (1) ultrasonic generator, (2) the "soni-cell", and (3) bowl shaped transducer.

Ultrasonic Generator. A RICH-ROTH "400" ultrasonic generator, manufactured by The General Ultrasonic Company, 1240 Main Street, Hardford 3, Conn., was used in this investigation. It is a general purpose, broad-band frequency generator intended to supply 400 watts of power to ultrasonic transducers at any point in the frequency range 10 kilocycles to 1.2 megacycles per second. In addition, it could also be used to excite transducers having input impedances that can vary from two ohms to 400 ohms anywhere in this frequency range.

The important controls of the generator are shown in Figure 6, page 72.

The Soni-cell. A RICH-ROTH soni-cell, type L-250, was used with the above ultrasonic generator. Essentially, it consists of a cylindrical barium titanate transducer with connections for cooling water outside the transducer. It is
Figure 6. RICH-ROTH "400" Ultrasonic Generator
copper lined and jacketed, hermetically sealed, water cooled, fully protected multi-frequency ultrasonic transducer. Important specifications are listed below:

**Transducer Type.** Piezoelectric, polycrystalline.

**Major Resonant Frequencies.**
- Low frequency: approximately 20 kc/sec
- High frequency: approximately 400 kc/sec

**Configuration.** Hollow cylinder.

**Treatment Chamber.** Cylindrically irradiated copper cylinder, seven inches deep, 2-1/2 inches outside diameter, open top, bottom drilled and tapped for 1/8-inch NPT hole for drainage or recirculation.
- Liquid capacity, approximately one pint.

**Cooling System.** Water cooled. Thermostat interrupts power if necessary to prevent overheating.

**Maximum Safe Temperature.** 90 °C.

**Overall Measurements.** Approximately seven inches in diameter, and nine inches high.

The important features of the L-250 type sonic-cell are shown in Figures 7 and 8, pages 74 and 75.
Figure 7. Cross-sectional View of the

RICH-ROTH Soni-cell L-250
Figure 8. Physical Features of Soni-cell L-250
Bowl Shaped Transducer. The bowl shaped transducer is manufactured by Brush Electronics Company, Cleveland, Ohio. It is a model No BU-305A, serial No 51B062, transducer mounted in a metal housing to facilitate electrical connections and safe handling. In Figure 9, page 77, is shown the unmounted bowl shaped transducer. The transducer was used in the evaluation of the ultrasonic probe.

Dialyzing Cell. No previous design was available for the dialyzing cell in the form to be used in this investigation. The development of the cell is outlined in the following sections.

Cylindrical cellophane tubing 1-1/8 inch outside diameter, 0.001 inch thick, and with an average pore diameter of 48 Angstroms was used as the permeable membrane. The major problems involved were: (1) location of inlet and outlet tubes for caustic solution, (2) closing of the bottom of cellophane tubing, and (3) size of the dialyzing cell.

Location of Inlet and Outlet Connections.
The inlet and outlet connections were located at the top of the cell. One end of the cellophane
Figure 9. The Unmounted Bowl Shaped Transducer
tubing was slipped on a pyrex glass tube, two inches long and 1-1/16 inch outside diameter, and which formed the top of the cell. Care was taken so that the edges of the glass tubing were smooth. This was necessary as otherwise the sharp edges of the tube would cut through the cellophane membrane. A rubber band was placed around that portion of the membrane which was slipped on the pyrex tube so as to keep it in place. To keep the membrane from slipping from the glass tubing when it was full, cotton cord (or twine) 1/16 inch thick was tied around that portion of the membrane which was on the glass tube.

The top of the pyrex glass tube was closed with a black, two hole rubber stopper. Through one hole passed a 5/16 inch outside diameter pyrex glass tube reaching almost to the bottom of the cell. Through the other hole passed another 5/16 inch pyrex glass tube which reached only up to the lower end of the rubber stopper. To make the joint between the rubber stopper and the glass tube (1-1/16 inch outside diameter) molten wax was poured around the joint and
allowed to solidify. A leak proof connection was easily obtained in this way.

Figure 10, page 80, shows various features of the dialyzing cell.

**Closing the Bottom of Dialyzing Cell.** The technique of closing the bottom part of the cellophane posed a big problem, as the whole surface of the dialyzing cell had to be perfectly smooth. Even slight crimps on the surface of the cell could not be tolerated because leaks would develop at these places when exposed to the ultrasonic field.

Various trials with different materials indicated that a rubber stopper could be used efficiently for closing the bottom of the cellophane tubing. The technique is described below.

The membrane was slipped on a one inch black rubber stopper as far as it will go. Then, an elastic rubber band, folded twice, was slipped on that part of the membrane which was on the stopper to give a tight hold. The rubber band was placed at about 1/8 inch below the end of the rubber stopper that was inside the membrane. To give
Figure 10. Dialyzing Cell
added strength, another rubber band was slipped on the rubber stopper in the same manner as the first one. Only, the second rubber band was at a distance of about 3/8 inch from the first rubber band, as shown in Figure 10, page 80. Although this method always yielded a leak proof cell, every time a new cell was made it was checked for leaks.

**Barium Titanate Probe.** The probe was designed to study intensity distribution of the transducers. In this investigation, the probe was used to map the intensity distribution in the cylindrical (soni-cell) and bowl shaped transducers. The details of construction are described below.

A small cylindrical piezoelectric transducer of barium titanate ceramic, 1/16 inch outside diameter and 1/16 inch in length was employed as the detector-converter of the sound pressure to alternating voltages. Figure 11, page 82, shows the various components and the assembled probe. The completed probe thus essentially consists of a barium titanate ceramic, a brass sleeve and a hypodermic needle (body not shown in Figure 11). The ceramic element was mounted on one end of the brass sleeve and the hypodermic needle on
Figure 11. The Barium Titanate Probe
the other. Duco cement was used to hold both the element and the needle in place in the brass sleeve. A wire was soldered to the body of the hypodermic needle and formed one lead. Another wire passing through the transducer, brass sleeve, and the hypodermic needle formed the other lead; from one end of this lead about 1/8 inch of insulation was removed and the individual wires in the lead spread out so as it would not pass easily through the transducer and also so that it would make a firm contact against the inner wall of the transducer.

One-sixteenth inch of the bare portion of the wire made firm contact with the inside of the transducer, while the remaining 1/16 inch held the wire in place with duco cement. This assembly was mounted in a lucite rod, 1/2 inch in diameter and five inches long, the rod serving as the holder.

**Equipment for Sono-dialysis.** The major pieces of equipment which were designed and constructed include the electrical and hydraulic panels, the angle iron supports for the solvent and solution tanks, and the arrangement for the measurement of voltage and current input to the transducer. The details are discussed in
"Design and Construction of an Ultrasonodialysis Cell" which is the title of a Bachelor of Science thesis (1956) in the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia, by Mr. S. Kent Snedegar who assisted the author in the construction phase of this investigation.

Method of Procedure

The method of procedure employed in this investigation is considered under the following headings:

(1) development of the dialyzing cell, (2) procedure for sono-dialysis, (3) mapping of intensity distribution in soni-cell, and (4) mapping of intensity distribution in bowl shaped transducer.

Development of the Dialyzing Cell. One of the major problems in this investigation was the design and construction of the dialyzing cell for the counter-current dialysis with ultrasonics. The factors taken into account in the development of the dialyzing cell were: (1) shape of the cell, (2) connections for inlet and outlet tubes, and (3) evaluation of dialyzing cell.
Shape of the Dialyzing Cell. The dialyzing cell was made in cylindrical shape, Figure 10, page 80, as it was planned to employ a cylindrical transducer for sono-dialysis studies. Diameter of the cellophane tubing and its length were limited by the dimensions of the cylindrical transducer (soni-cell). As the diameter and length of the soni-cell were 2-1/2 and 7-1/4 inches, respectively, Figure 2, page 9, the corresponding figures of 1-1/8 inch and seven inches were chosen for the dialyzing cell. Another reason was that cellophane tubing of 1-1/8 inch was easily available.

Connections for Inlet and Outlet Tubes. Inlet and outlet tubes in the dialyzing cell were located in such a way that the caustic feed entered at the bottom of the dialyzing cell and left from the outlet tube at the top of the dialyzing cell. Glass tees were placed between the line from the caustic feed tank and inlet to the dialyzing cell, and between the outlet from the dialyzing cell to the raffinate exit. This arrangement is shown in Figure 12, page 86. By this device a constant flow, that is the volume of caustic feed
Figure 12. Arrangement Showing the Inlet and Outlet Connections to the Dialyzing Cell
delivered by the metering device (a capillary tube in this case), could be maintained through the dialyzing cell.

**Evaluation of the Dialyzing Cell.** In order to test if reproducible results could be obtained for the countercurrent dialysis without insonation various tests were made with the same dialyzing cell. It was found that the results varied from one test to another. Later, it was learned from the literature that cellophane swells in water and caustic solutions, and that its porosity increases. However, most of the swelling and increase in porosity takes place in the first 15 to 20 minutes of the treatment. When dialysis tests were made with the pretreated cellophane membrane, reproducible results were obtained. Hence, in all later experiments the dialyzing cell was always pretreated with caustic solution for one-half hour.

**Procedure for Sono-Dialysis.** Here, the term sono-dialysis is employed to denote the study of dialysis with insonation. In this investigation water was used as the outer liquid or solvent for dialysis and caustic
solution as solute. A fine bore capillary (diameter 0.25 to 0.75 millimeter) was used as a metering device for caustic solution as well as for water. The flow rates for caustic solution and water were five and eleven milliliters per minute, respectively. These values were selected from a study of the literature.

The inlet and outlet arrangements for water in the soni-cell are shown in Figure 13, page 89. As is seen, the water enters at the top in the soni-cell and leaves at the bottom through a glass tee. The function of the glass tee is very important here. It is known from the operating instructions of the soni-cell that the level of the liquid in it must always be at least one inch from the top of the soni-cell. In this investigation, the level was always maintained at one-half inch from the top of the soni-cell. The tee was used to break the siphon effect and to maintain a constant level of the liquid in the soni-cell.

The operating procedure for sono-dialysis is discussed under the following headings: (1) starting procedure, (2) procedure during the test, (3) closing procedure, and (4) analytical procedure.
Figure 13. Arrangement Showing the Inlet and Outlet Connections to the Soni-cell
Starting Procedure. The starting procedure can further be divided into the following steps:

1. filling up of water and caustic tanks,
2. preparation and placement of dialyzing cell, and
3. start up procedure for ultrasonic generator.

Filling Up of Water and Caustic Tanks.
A 50-gallon aluminum tank was used as the water tank and a one-gallon glass carboy, with an opening at the bottom, for caustic storage. A scale was pasted on the glass carboy to indicate the level of the liquid.

The glass carboy was closed with a two-hole rubber stopper. The stem of a 250-milliliter separating funnel passed through one hole and through the other passed a tube which was connected to an apparatus for delivery of moisture and carbon dioxide-free air. The liquid level was maintained between the third and fourth scale divisions. This difference of one scale division was equivalent to one-half inch. In other words, the
level variation for all tests was maintained within one-half inch (see Figure 14, page 92).

Placement of the Dialyzing Cell. The dialyzing cell was prepared as discussed earlier. It was filled with caustic solution and placed in the soni-cell, and clamped. It was connected with the inlet and outlet lines for caustic as shown in Figure 12, page 86. The outlet line was closed with a hosecock clamp at position C, the clamp at position D opened, and the caustic solution allowed to enter the dialyzing cell. All of these positions refer to Figure 13, page 89. Precaution was taken that no air bubbles remained in the caustic inlet line or in the dialyzing cell. When the inlet tube and the cell became completely filled with caustic, the caustic started rising in tubes A and B. When the level had arisen about three-fourths of the tube length B, the tube at A was closed tightly with a clamp, and the
Figure 14. The Arrangement to Obtain Carbon Dioxide and Moisture Free Air, and the Glass Carboy Used as Caustic Storage
clamp at position C was opened, and the liquid was allowed to flow out from the exit tube.

The caustic was allowed to run through this set up for about four to five minutes and then clamp at A was opened. This insured that all the caustic line was full and did not have any air bubbles, that the same constant amount of caustic which flowed out from the capillary tube, passed through the dialyzing cell and out from the exit tube; that is, a constant flow was maintained.

The next step was to fill the soni-cell with distilled water until the level in it reached one-half inch from the top. This level was regulated by the manipulation of the height of the glass tee D, Figure 13, page 89. In this investigation, the height of the horizontal arm of the tee was 15 inches from the top of the table to the top of the horizontal arm.

The valve V-I was then opened and water allowed to enter the soni-cell at the top through the tube E, care being taken that no air bubbles remained in the water line.
Start Up Procedure for the Ultrasonic Generator. The start up procedure for the RICH-ROTH type "400" ultrasonic generator was as follows:

1. Tap water, for cooling the transducer, was allowed to flow through the soni-cell. The flow rate was adjusted at approximately 250 milliliters per minute. This was very important as the temperature in the soni-cell should not be allowed to rise above 90 °C, that is, above the Curie point; otherwise, the transducer will lose its piezoelectric property.

2. Matching network was placed between the outlet of the ultrasonic generator and the inlet of the soni-cell, as shown in Figure 15, page 95.

3. The main switch on the electrical panel, and then the on-off switch on the ultrasonic generator, were turned on.

4. About five minutes were allowed for the warm up time. The power control was turned to three and tuning adjusted until
Figure 15. Connections for the Matching Network at Low Frequencies
the transducer resonance was indicated either (1) by the tuning eye, (2) by the noise of cavitation, or (3) by bubbles or movement in the liquid with which the transducer was in contact. It was found that when the tuning pointed to 57 (for 10 to 25 milocycle range) and 87 (for 145 to 500 kilocycle range, no matching unit being used in this case), maximum agitation was obtained in the soni-cell indicating that resonance was attained. Then, the power control was moved to the required value under investigation.

5. The electric timer was started to register the duration of the test.

Procedure During Test. After the experiment was started, the procedure during the test involved the following points:

1. During the experiment the level of the caustic solution flowing out from the dialyzing cell through glass tee B, Figure 12, page 86, was regulated. So long as the level remained stationary the system was operating satisfactorily, but as soon as a leak developed in the dialyzing
cell, the level in the glass tee dropped immediately. Dropping of the level in the glass tee was an indication that the experiment should be stopped.

2. Samples were taken at 10, 20, 40, 60, 80, 100, and 120 minutes. If a leak appeared in the dialyzing cell before 20 minutes the test was cancelled and the experiment started all over again. This was necessary as at least two points were required to calculate the equilibrium values for the raffinate (spent caustic solution leaving the dialyzing cell) and the extract (the solution leaving the soni-cell through the glass tee E, Figure 13, page 89).

3. Temperature of the liquid in the soni-cell was recorded each time a sample was taken.

4. After the experiment was over, the tuning and power controls were moved to zero position and a radio frequency ammeter (range 0 to 5 amperes) connected between the matching network and the soni-cell. The power and tuning controls were moved back to the position where they were during the experiment and the radio frequency current
read on the ammeter. This value was used in the
calculation of power delivered at the transducer
by the generator.

_Closing Procedure._ The closing procedure
involved the following sequence of steps:

1. Valve V-1 was closed to shut off the
supply of water, and the tubing from the caustic
tank was closed with a hosecock clamp.

2. The inlet and outlet tubes to the
dialyzing cell were disconnected.

3. The dialyzing cell was unclamped, taken
out from the soni-cell, and observed for any leaks.

4. The soni-cell was filled again with dis­
tilled water so that the level of the liquid was
one-half inch from the top of the soni-cell. The
tuning and power controls were moved to the posi­
tion that they were during the experiment. Inten­
sity measurements were made at a depth of two
inches from the top of the liquid level, using
the barium titanate probe, according to the
scheme shown in Figure 16, page 99. The technique
of using the probe is described under "Mapping of
Intensity Distribution in Soni-cell."
TOP VIEW

CYLINDRICAL TRANSDUCER (SONI-CELL)

NOTE 1: AA, BB, CC, AND DD ARE TERMED DIAMETERS

2: NUMBERS 1, 2, 3, 4, AND 5 INDICATE POSITIONS
   AT WHICH INTENSITY MEASUREMENTS WERE MADE

Figure 16. Scheme for Intensity Measurements
   in the Soni-cell
Analytical Procedure. Analytical procedure includes the method of taking samples and their analysis.

As has been stated previously, samples were collected at 10, 20, 40, 60, 80, 100, and 120 minutes after the experiment was started. Samples were collected for one and one-half minutes at the required time in a 15-milliliter sample bottle.

Standard titrimetric methods were used for the analysis. Two standard hydrochloric acid solutions of 0.0495 N and 0.0104 N were prepared to titrate against the raffinate and the extract from the dialyzing cell and the soni-cell, respectively. Methyl orange was used as indicator.

Mapping of Intensity Distribution in Soni-cell. This part of the investigation consists of the mapping of the intensity distribution in the soni-cell. It has been mentioned already that a barium titanate probe was designed and constructed for the measurements of the ultrasonic intensity in the medium directly. Intensity distribution of the soni-cell was mapped at power levels of four, five, and six
as located on the ultrasonic generator, and at frequency ranges of 10 to 25 kilocycles (frequency 22 kilocycles) and 145 to 500 kilocycles (frequency 420 kilocycles). The medium was distilled water.

**Setting Up of Soni-cell.** The following sequence of operations was observed to set up the soni-cell for intensity measurements.

1. Soni-cell was filled with distilled water until the liquid level was one-half inch from the top of the soni-cell.
2. Cooling water was allowed to flow through the soni-cell.
3. Ultrasonic generator was turned on and tuned as described on page 94, under the heading, "Start Up Procedure for Ultrasonic Generator."

**Horizontal and Vertical Mapping of the Intensity Distribution.** Four diameters were marked on the top of soni-cell as shown in Figure 16, page 99. The diameters were termed AA, BB, CC, and DD. Arrows were marked on these diameters to indicate the direction in which measurements were made. The marks were scratched lightly on the top of soni-cell.
Next, the leads from the barium titanate probe were connected, through a coaxial cable, to a vacuum tube voltmeter. Also, a one-half watt, one megohm resistance was connected in parallel at the terminals of the vacuum tube voltmeter. This was done because exploratory work had indicated that addition of the resistance made the readings on the vacuum tube voltmeter more stable than without the resistance. The on-off switch on the vacuum tube voltmeter was turned on, and a warm up period of five minutes was allowed before any observations were taken.

Next, the probe was mounted in a clamp and stand arrangement as shown in Figure 17, page 103. Measurements of intensity were made at five points, at a distance of one-half inch from each other, along the diameters AA, BB, CC, and DD. These measurements were repeated at the depths of one, two, three, four, five, and six inches from the top of the liquid level in the soni-cell. In all, 120 measurements were made at one power level of the ultrasonic generator. Three such power
Figure 17. Clamp and Stand Arrangement for Intensity Measurements with the Probe
levels corresponding to the power dial readings of four, five, and six were used. These three intensities were studied at two frequency levels, range 10 to 25 kilocycles (actual frequency = 22 kilocycles), and 145 to 500 kilocycles (actual frequency = 420 kilocycles).

**Closing Procedure.** The probe was taken out of the soni-cell and de-clamped. The tip of the probe was dried carefully with a filter paper, and the probe placed in its box. The on-off switch on the vacuum tube voltmeter was turned off.

The closing procedure for the ultrasonic generator was the same as given on page 98 under the heading, "Closing Procedure."

**Mapping of Intensity Distribution in Bowl Shaped Transducer.** This section deals with the mapping of intensity distribution in the field of a bowl shaped transducer. The unmounted transducer is shown in Figure 9, page 77. The same barium titanate probe, which was employed to measure intensity in the soni-cell, was used in this case also. The procedure is described below.
Setting Up of the Transducer. The following sequence of operations was observed to set up the bowl shaped transducer for intensity measurements.

1. The mounted transducer without transparent spray shield, Fig 18, page 106, was filled with distilled water until the liquid level was one-half inch from the top of the metallic "adaptor sleeve."

2. Tap water was allowed to flow through the cooling coils of the mounted transducer.

3. The transducer was connected to the RICH-ROTH ultrasonic generator (no matching network included). The ultrasonic generator was turned on and tuned as described on page 94, under the heading, "Start Up Procedure for the Ultrasonic Generator."

Horizontal and Vertical Mapping of the Intensity Distribution. The scheme of the mapping of intensity distribution in a bowl shaped transducer was the same as shown in Figure 16, page 99. The apparatus was arranged in such a way that the diameter EE passed through
Figure 18. Mounted Bowl Shaped Transducer
the center of the electrical inlet to the transducer as shown in Figure 18, page 106.

The remainder of the procedure was the same as described on pages 101 and 102, under the heading, "Horizontal and Vertical Mapping of the Intensity Distribution," and page 104, under the heading, "Closing Procedure," with the following exceptions:

1. Only one frequency, namely 420 kilocycles per second, was employed for intensity determinations.

2. Intensity measurements were made at the depths of 1/2, 1, 1-1/2, 2, 2-1/2, and 3 inches from the top of the liquid level in the transducer.
Data and Results

The data and results obtained in this investigation are presented in this section. They are described under the following headings: (1) intensity measurements in a cylindrical transducer (or soni-cell), (2) intensity measurements in a bowl shaped transducer, and (3) the overall mass transfer coefficients in the sono-dialysis of caustic solution in the presence of absence of ultrasonics.

Intensity Measurements in a Cylindrical Transducer.
The data and results obtained for the intensity measurements in the soni-cell, using distilled water as the medium and at frequencies of 22 and 420 kilocycles per second, are presented in Table V, page 115. The first column shows the depth at which measurements were made. At each of the four diameters, AA, BB, CC, and DD, intensity measurements were made at five positions.

The data so obtained have been expressed graphically to help understand the intensity measurements. A brief description of the graphical representation follows.
Representations of Intensity Measurements at Horizontal Levels. The intensity values have been presented in this fashion in order to show the intensities horizontally at various points (five points) at depths of one, two, three, four, five, and six inches from the top of the liquid level in the soni-cell. The graphs are shown in Figures 19, 20, 21, 22, 23, and 24, pages 116, 117, 118, 119, 120, and 121. Each circle represents a horizontal section at the depth noted beside it. The values in the circle are the intensity values in volts as measured by the barium titanate probe and the vacuum tube voltmeter arrangement.

Vertical Representation of Intensity Distribution at the Transducer. In this case, the intensity distribution has been mapped vertically at the transducer with the probe. As is seen from Figures 25, 26, 27, 28, 29, and 30, pages 122, 123, 124, 125, 126, and 127, the ordinate represents the depth at which measurements were made and the abscissa represents the position of measurement as well as intensity in volts as
indicated by the vacuum tube voltmeter. These positions have been labeled after the positions of the arms of a clock. Diameter BB, at the top, has been ascribed the position corresponding to 12.00 at the clock (see Figure 16, page 99) and then going in the clockwise direction as 1.30, 3.00, 4.30, 6.00, 7.30, 9.00, and 10.30. At each of these positions, intensity measurements were made corresponding to the depths of one, two, three, four, five, and six inches.

**Vertical Representation of Intensity Distribution at the Intermediate Position.** The intermediate position also corresponds to the position of the membrane. This set of observations was made at a distance of one-half inch from the cylindrical transducer. The vertical measurements of intensity have been presented in the same manner as in the previous section. The plotted data are shown in Figures 31, 32, 33, 34, 35, and 36, pages 128, 129, 130, 131, 132, and 133.
Vertical Representation of Intensity Distribution at the Center (of the Soni-cell). These observations were taken at the center of the cylindrical transducer and at each diameter, AA, BB, CC, and DD. Figures 37, 38, 39, 40, 41, and 42, pages 134, 135, 136, 137, 138, and 139, show the graphical representation of the data so obtained.

Ranges of Intensity Distribution at the Transducer, at the Intermediate Position, and at the Center. In order to see the range of intensity measurements at the transducer, at the intermediate position, and at the center, the data were plotted according to the scheme shown in Figures 43, 44, 45, 46, 47, and 48, pages 140, 141, 142, 143, 144, and 145. This arrangement indicates the extent of variation of the intensity values at the above three positions.

Intensity Measurements in the Bowl Shaped Transducer. The intensity values obtained in the bowl shaped transducer are presented in Table VI, page 146. The table shows the values of intensity at three power levels, four, five, and six, as indicated on the
ultrasonic generator, and at a frequency of 420 kilocycles per second. The scheme of presentation is similar to measurements of intensity at horizontal levels with the cylindrical transducer.

The intensity measurements so obtained are plotted graphically and are described below.

**Representation of Intensity Measurements at Horizontal Levels.** The intensity values have been presented in this manner in order to show the intensities horizontally at various points (five points) at depths of 1/2, 1, 1-1/2, 2, 2-1/2, and 3 inches from the top of the liquid level in the transducer. The graphs are shown in Figures 49, 50, and 51, pages 147, 148, and 149. Each circle represents a horizontal section at the depth noted beside it. The values in the circle are the intensity values in volts as measured by the barium titanate probe and the vacuum tube voltmeter arrangement.

**Representation of Intensity Values in the Bowl Shaped Transducer.** In this case the data have been plotted in Figures 52, 53, and 54, pages 150, 151, and 152, to indicate the
intensity profile in the transducer. The abscissa represents the positions (at five positions) at which intensity measurements were made at each of the four diameters, AA, BB, CC, and DD, and the ordinate represents the intensity values in volts. The six curves for each diameter are each at 1/2, 1, 1-1/2, 2, 2-1/2, and 3 inches depth from the top of the liquid level in the transducer.

Overall Mass Transfer Coefficients in Sonodialysis. This section deals with the determination of the overall mass transfer coefficients in the dialysis of 0.24 N caustic solution in the presence and absence of ultrasonics. The dialysis was carried out under the following conditions in the presence of ultrasonics:

Water flowrate : 11.0 ml/min
Caustic flowrate : 5.0 ml/min
Output impedance (on the generator) : D
Water flowrate (cooling water through the soni-cell) : 250 ml/min
Sono-dialysis data are presented in Table VII, page 153. The table also includes the data of the test in the absence of ultrasonics.

Overall mass transfer coefficients are calculated at the power levels studied, and are presented in Table VIII, page 154, with the corresponding intensity levels. Also, overall mass transfer coefficients were plotted against the corresponding intensity values as is shown in Figure 55, page 155.
### TABLE V

**Intensity Measurements in a Cylindrical Transducer**

(Soni-Cell) at 22 and 420 Kilocycles per Second

**Using a Barium Titanate Probe**

(See Pocket in Appendix)
Figure 19. Intensity Distributions at Various Horizontal Levels

(Power Dial 4  Freq. 22 kc/sec)
Figure 20. Intensity Distributions at Various Horizontal Levels
(Power Dial 5    Freq. 22 kc/sec)
Figure 21. Intensity Distributions at Various Horizontal Levels
(Power Dial 6  Freq. 22 kc/sec)
Figure 22. Intensity Distributions at Various Horizontal Levels

(Power Dial 4     Freq. 420 kc/sec)
Figure 23. Intensity Distributions at Various
Horizontal Levels

(Power Dial 5    Freq. 420 kc/sec)
Figure 24. Intensity Distributions at Various Horizontal Levels

(Power Dial 6  Freq. 420 kc/sec)
Figure 25. Intensity Distribution at Various Depths at the Transducer

(Power Dial 4  Freq. 22 kc/sec)
Figure 26. Intensity Distribution at Various Depths at the Transducer

(Power Dial 5    Freq. 22 kc/sec)
Figure 27. Intensity Distribution at Various Depths at the Transducer

(Power Dial 6       Freq. 22 kc/sec)
Figure 28. Intensity Distribution at Various Depths at the Transducer

(Power Dial 4       Freq. 420 kc/sec)
Figure 29. Intensity Distribution at Various Depths at the Transducer

(Power Dial 5       Freq. 420 kc/sec)
Figure 30. Intensity Distribution at Various Depths at the Transducer
(Power Dial 6       Freq. 420 kc/sec)
Figure 31. Intensity Distribution at Various Depths at the Membrane

(Power Dial 4  Freq. 22 kc/sec)
Figure 32. Intensity Distribution at Various Depths at the Membrane
(Power Dial 5  Freq. 22 kc/sec)
Figure 33. Intensity Distribution at Various Depths at the Membrane

(Power Dial 6      Freq. 22 kc/sec)
Figure 34. Intensity Distribution at Various Depths at the Membrane

(Power Dial 4       Freq. 420 kc/sec)
Figure 35. Intensity Distribution at Various Depths at the Membrane

(Power Dial 5  Freq. 420 kc/sec)
Figure 36. Intensity Distribution at Various Depths at the Membrane

(Power Dial 6  Freq. 420 kc/sec)
Figure 37. Intensity Distribution at Various Depths at the Center

(Power Dial 4  Freq. 22 kc/sec)
Figure 38. Intensity Distribution at Various Depths at the Center

(Power Dial 5       Freq. 22 kc/sec)
Figure 39. Intensity Distribution at Various Depths at the Center

(Power Dial 6 Freq. 22 kc/sec)
Figure 40. Intensity Distribution at Various Depths at the Center

(Power Dial 4   Freq. 420 kc/sec)
Figure 41. Intensity Distribution at Various Depths at the Center

(Power Dial 5 Freq. 420 kc/sec)
Figure 42. Intensity Distribution at Various Depths at the Center

(Power Dial 6       Freq. 420 kc/sec)
Figure 43. Intensity Distribution Ranges at Various Depths

(Power Dial 4    Freq. 22 kc/sec)
Figure 44. Intensity Distribution Ranges at Various Depths

(Power Dial 5       Freq. 22 kc/sec)
Figure 45. Intensity Distribution Ranges at Various Depths
(Power Dial 6  Freq. 22 kc/sec)
Figure 46. Intensity Distribution Ranges at Various Depths

(Power Dial 4      Freq. 420 kc/sec)
Figure 47. Intensity Distribution Ranges at Various Depths
(Power Dial 5 Freq. 420 kc/sec)
Figure 46. Intensity Distribution Ranges at Various Depths

(Power Dial 6 Freq. 420 kc/sec)
TABLE VI

Intensity Distribution in a Bowl Shaped Transducer at Various Depths

(See Pocket in Appendix)
Figure 49. Intensity Distribution at Various Horizontal Levels in the Bowl Shaped Transducer
(Power Dial 4 \hspace{1cm} \text{Freq.} 420 \text{ kc/sec})
Figure 50. Intensity Distribution at Various Horizontal Levels in the Bowl Shaped Transducer

(Power Dial 5    Freq. 420 kc/sec)
Figure 51. Intensity Distribution at Various Horizontal Levels in the Bowl Shaped Transducer

(Power Dial 6   Freq. 420 kc/sec)
Figure 52. Intensity Distribution at Various Depths in a Bowl Shaped Transducer

(Power Dial 4   Freq. 420 kc/sec)
Figure 53. Intensity Distribution at Various Depths in a Bowl Shaped Transducer

(Power Dial 5  Freq. 420 kc/sec)
Figure 54. Intensity Distribution at Various Depths in a Bowl Shaped Transducer

(Power Dial 6  Freq. 420 kc/sec)
TABLE VII

Sono-Dialysis of a Caustic Solution at Various Intensities

(See Pocket in Appendix)
TABLE VIII

Overall Mass Transfer Coefficients at Various Intensities

(See Pocket in Appendix)
Figure 55. Overall Mass Transfer Coefficients Versus Ultrasonic Intensity in Sono-Dialysis
Sample Calculations

The sample calculations for this investigation are described in this section. Sono-dialysis of caustic solutions involves the calculation of the following quantities: (1) overall mass transfer coefficients, and (2) caustic balance.

Overall Mass Transfer Coefficients. The determination of overall mass transfer coefficients involves the calculation of the following steps: (1) equilibrium values for extract and raffinate, (2) extract and raffinate concentration, (3) log-mean concentration difference, (4) area of the dialyzing cell, and (5) weight of material passing through the membrane per unit time.

Equilibrium Values for Extract and Raffinate.

It has been mentioned earlier that leaks were produced in the cellophane membrane when it was placed in the field of ultrasonics. Experiments indicated that a minimum of two hours were required to attain equilibrium in dialysis with ultrasonics. However, earlier work also showed that if reciprocal of time were plotted against the reciprocal of corresponding titer value, a
straight line was obtained. This fact was used in the determination of the equilibrium values for the extract and raffinate.

Figures 56, 57, 58, 59, and 60, pages 158, 159, 160, 161, and 162, show the plot of reciprocal of time versus reciprocal of titer value.

The reciprocal values are presented in Table IX, page 163. The equilibrium values so obtained are presented in Table X, page 164. For example, for the test with power dial reading three, the equilibrium values for the extract and raffinate are 23.3 milliliters and 15.4 milliliters, respectively.
Figure 56. Reciprocals of Time versus Titer Values for the Calculation of Equilibrium Values of Extract and Raffinate

(Power Dial 2 Freq. 22 kc/sec)
Figure 57. Reciprocals of Time versus Titer Values for the Calculation of Equilibrium Values of Extract and Raffinate

(Power Dial 3 Freq. 22 kc/sec)
Figure 53. Reciprocals of Time versus Titer Values for the Calculation of Equilibrium Values of Extract and Raffinate

(Power Dial 4    Freq. 22 kc/sec)
Figure 59. Reciprocals of Time versus Titer Values for the Calculation of Equilibrium Values of Extract and Raffinate

(Power Dial 5 Freq. 22 kc/sec)
Figure 60. Reciprocals of Time versus Titer Values for the Calculation of Equilibrium Values of Extract and Raffinate

(Power Dial 6 Freq. 22 kc/sec)
### TABLE IX

**Reciprocals of Time and Titer Values for the Calculation of Equilibrium Values of Extract and Raffinate**

<table>
<thead>
<tr>
<th>Time (T)</th>
<th>Power Level: 2</th>
<th>Power Level: 3</th>
<th>Power Level: 4</th>
<th>Power Level: 5</th>
<th>Power Level: 6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/T</td>
<td>Extract</td>
<td>Raffinate</td>
<td>Extract</td>
<td>Raffinate</td>
</tr>
<tr>
<td></td>
<td>min⁻¹ ml⁻¹</td>
<td>ml⁻¹</td>
<td>ml⁻¹</td>
<td>ml⁻¹</td>
<td>ml⁻¹</td>
</tr>
<tr>
<td>min</td>
<td>10</td>
<td>0.10</td>
<td>0.152</td>
<td>0.146</td>
<td>0.133</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.05</td>
<td>0.100</td>
<td>0.165</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.025</td>
<td>--</td>
<td>--</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.017</td>
<td>--</td>
<td>--</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.013</td>
<td>--</td>
<td>--</td>
<td>0.043</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.001</td>
<td>--</td>
<td>--</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>0.008</td>
<td>--</td>
<td>--</td>
<td>0.042</td>
</tr>
</tbody>
</table>
TABLE X

Equilibrium Titer Values for the Extract and Raffinate in the Sono-Dialysis Experiments

<table>
<thead>
<tr>
<th>Power Control Level</th>
<th>Extract(^a)</th>
<th>Raffinate(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>14.5</td>
<td>18.3</td>
</tr>
<tr>
<td>2</td>
<td>17.25</td>
<td>14.5</td>
</tr>
<tr>
<td>3</td>
<td>23.8</td>
<td>15.4</td>
</tr>
<tr>
<td>4</td>
<td>28.6</td>
<td>14.9</td>
</tr>
<tr>
<td>5</td>
<td>23.8</td>
<td>14.5</td>
</tr>
<tr>
<td>6</td>
<td>22.2</td>
<td>14.3</td>
</tr>
</tbody>
</table>

\(^a\) Titrated against 0.0104 N HCl solution.

\(^b\) Titrated against 0.0495 N HCl solution.
Extract and Raffinate Concentration. Hydrochloric acid of 0.0104 N and 0.0495 N was used to titrate against five milliliters each of the extract and raffinate, respectively. The concentrations of the extract and raffinate for the test under consideration are:

\[
\text{Extract} = \frac{23.8 \times 0.0104}{5} = 0.05 \text{ N}
\]

\[
\text{Raffinate} = \frac{15.4 \times 0.0495}{5} = 0.1525 \text{ N}
\]
Log-Mean Concentration Difference. Log-mean concentration difference was necessary to calculate, as equation 7, page 18, was used in the calculation of overall mass transfer coefficients. The concentration of caustic solution entering the dialyzing cell was 0.24 N. The determination of log-mean concentration difference is as follows:

\[
\Delta C_{1m} = \frac{\Delta C_1 + \Delta C_2}{2.303 \times \log (\Delta C_1/\Delta C_2)}
\]

where:

\( \Delta C_{1m} \) = log-mean concentration difference, N

\( \Delta C_1 \) = concentration difference between the caustic entering the dialyzing cell and extract leaving the soni-cell, N

\( \Delta C_2 \) = concentration difference between the caustic leaving the dialyzing cell (raffinate) and water entering the soni-cell, N
For the test under concentration:

\[ \Delta C_1 = 0.24 - 0.05 = 0.19 \text{ N} \]

\[ \Delta C_2 = 0.1525 - 0.0 = 0.1525 \text{ N} \]

and

\[ \Delta C_{lm} = \frac{0.1900 - 0.1525}{2.3 \times \log (0.1900/0.1525)} \]

\[ = \frac{0.0375}{2.3 \times 0.0956} = 0.1705 \text{ N} \]

The log-mean concentration was expressed in grams per milliliter instead of Normality, that is:

\[ \Delta C_{lm} = 0.1705 \times \frac{10}{1000} = 0.00682 \text{ gm/ml} \]
Area of the Membrane. It has been stated earlier that the length of the dialyzing cell was seven inches. As seen from Figure 10, page 80, this includes the length (one inch) of rubber stopper used to close the bottom of the dialyzing cell. The actual useful dialyzing length is, therefore, six inches.

The area of the dialyzing cell, as the cell is cylindrical, is given by the equation:

\[ A = \pi D L \]

where:

- \( A \) = area of the membrane, sq cm
- \( D \) = diameter of the membrane, cm
- \( L \) = length of the membrane, cm

The area of the membrane is:

\[ = 3.14 \times \left( \frac{9}{8} \times 2.54 \right) \times (6.0 \times 2.54) \]

\[ = 137 \text{ sq cm} \]
Weight of Material Passing Through the Membrane per Unit Time. The weight of the material passing through the membrane is the same as the equilibrium concentration of the extract from the soni-cell multiplied by the flowrate of the extract. As the extract leaves the soni-cell at the same rate as water enters it, and as the flowrate of water is 11 milliliters per minute, the required extract flowrate is, therefore, 11 milliliters per minute. For the test under consideration,

\[ W = \text{weight of the material passing through the membrane per unit time is,} \]

\[ = (0.05 \times \frac{40}{1000} \text{ gm/ml}) \times (11 \text{ ml/min}) \]

\[ = 0.220 \text{ gm/min} \]
Overall mass transfer coefficients were calculated from the equation 7, page 18. For the test under consideration $K$, the overall mass transfer coefficient (or dialysis constant) is:

$$K = \frac{0.220}{137 \times 0.00682} = 0.220 = 0.2354 \text{ cm/min}$$

Table VIII, page 154, shows the values of the overall mass transfer coefficients and the corresponding ultrasonic intensities as measured from the product of the square of radio frequency current at the transducer multiplied by the impedance. The impedance was calculated from the information given in the manufacturer's instructions. According to this information, the impedance varies in the range from 2.5 to 320 ohms increasing in eight geometrical progression steps. As the output impedance was on D on the ultrasonic generator which was the fourth step, the impedance is, therefore, 20 ohms.
Caustic Balance. Caustic balance was made for all of the six tests. The results are presented in Table XI, page 172, which also includes the material balance for the test made in the absence of ultrasanics. A sample calculation for the test under consideration is presented below:

Caustic in per hour = 0.24 x \( \frac{40}{1000} \) x 300 gm/hr

= 2.88 gm/hr (caustic flowrate is 5 ml/min)

Caustic out per hour is calculated as follows:

\[
\text{caustic out} = \text{caustic out in extract} + \text{caustic out in raffinate}
\]

\[
= (0.05 x \frac{40}{1000} x 660) + (0.1525 x \frac{40}{1000} x 300)
\]

= 3.15 gm/hr
### TABLE XI

**Material Balance for the Sono-Dialysis of Caustic Solutions**

<table>
<thead>
<tr>
<th>Power Control Level</th>
<th>Caustic In gm/hr</th>
<th>Caustic Out gm/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>2.88</td>
<td>2.9784</td>
</tr>
<tr>
<td>2</td>
<td>2.88</td>
<td>2.6808</td>
</tr>
<tr>
<td>3</td>
<td>2.88</td>
<td>3.15</td>
</tr>
<tr>
<td>4</td>
<td>2.88</td>
<td>3.354</td>
</tr>
<tr>
<td>5</td>
<td>2.88</td>
<td>3.048</td>
</tr>
<tr>
<td>6</td>
<td>2.88</td>
<td>2.9256</td>
</tr>
</tbody>
</table>
IV. DISCUSSION

This section deals with the discussion of the results obtained in the mapping of intensity distributions in cylindrical and bowl shaped transducers, and in the determination of overall mass transfer coefficients (or dialysis constants) in the sono-dialysis of 0.24 N caustic solution.

The discussion is divided into the following sections: (1) barium titanate probe, (2) intensity measurements in the soni-cell (cylindrical transducer), (3) intensity measurements in the bowl shaped transducer, and (4) sono-dialysis of 0.24 N caustic solution.

Barium Titanate Probe

Generally, direct measurements of sonic intensities at ultrasonic frequencies have been always a problem. Standard equipment is available, such as the sound level meter, to measure the absolute intensity of sound waves at frequencies in the audible range. However, at higher frequencies the problem becomes more complicated. In earlier investigations,
it has been a practice to consider the product of plate amperes and voltage of ultrasonic generator as the relative measure of sonic intensity. In an earlier investigation at Virginia Polytechnic Institute, the sonic intensity was measured at the transducer instead of the usual plate current-voltage product. The intensity at the transducer was determined by measuring the radio frequency voltage at the transducer with a vacuum tube voltmeter and dividing the square of this voltage by the impedance of the transducer. In the present investigation an attempt has been made to measure directly sonic intensity at the designated point.

A probe was designed and constructed to measure sonic intensity directly at a designated point. The probe essentially consists of a tiny cylindrical barium titanate transducer (diameter 1/16 inch, length 1/16 inch) which was used as the detector-convertor of the sonic pressure developed by the ultrasonic waves. The small size of the transducer was essential to avoid any diffraction effects in the sonic field, and also to greatly facilitate the measurement of intensities.
without creating any disturbance in the ultrasonic field.

The probe characteristics and performance are discussed under the following headings: (1) probe characteristics, (2) operation of the probe, and (3) mapping of the intensities by the probe.

**Probe Characteristics.** The basic requirements of a good working standard of sound pressure measurement (probe in this case) is that it should give an exact quantitative reproduction of sound pressure wave as it existed at a specific point before the probe was introduced. In the present investigation, the alternating voltages generated by the detector-convertor barium titanate transducer, which acts like a microphone, were measured by connecting the leads from the probe to a vacuum tube voltmeter. At this stage, it is not claimed that the intensity being measured is the absolute intensity at that point. Rather, it is considered that the values of intensity indicated are only the relative values. The same arrangement would yield true absolute intensities once the probe is calibrated. For the present the values indicated on
the vacuum tube voltmeter were read in volts and the intensity expressed as such in volts.

As has been mentioned earlier, most of the early intensity measurements were made indirectly, for example, by multiplying the plate current by the plate voltage. As far as is known to the author, this is the first time an attempt has been made to employ a probe to map the intensities in sonic fields in which some process or operation (sono-dialysis in this case) is to be studied. These measurements have shown that direct measurements of intensity are essential in the study of intensity dependent phenomena (or processes).

**Operation of the Probe.** It was found that in order to obtain stable readings on the vacuum tube voltmeter a one megohm, one-half watt resistance was connected in parallel at the terminals of the vacuum tube voltmeter. Also, the probe was clamped to obtain stability (see Figure 17, page 109).

The measurements made on the cylindrical transducer (soni-cell) and the bowl shaped transducer indicate that the probe was sensitive to differentiate between the intensities at power control levels of four, five, and six on the RICH-ROTH ultrasonic
generator. This is borne out clearly from Figures 19 through 24, pages 116 through 121, and Figures 49 through 51, pages 147 through 149, respectively. Values at each horizontal level are different and increase as the depth increases. It is seen that at the same power control level but at different depths the intensity values are different. This difference in intensity values is brought out very clearly when the intensity is plotted against various depths. See Figures 25 through 42, pages 122 through 139 for the cylindrical transducer, and Figures 52 through 54, pages 150 through 152, for the bowl shaped transducer.

**Mapping of Intensities by Probe.** The probe has been found to be very useful in mapping of the intensities. This has been proved amply by the measurements made in the cylindrical and bowl shaped transducers where certain interesting points have been brought out which were not known previously. These points are discussed under the intensity measurements in cylindrical and bowl shaped transducers, respectively.
A greater insight into the effects of ultrasonics can be obtained than was hitherto possible, because with the probe actual measurements in the sonic field can be made and a picture of the field intensity distribution obtained. The knowledge of the actual intensity distribution in a sonic field does not leave room for any assumptions about the field distribution.

It is considered that the quantitative mapping of a sonic field directly with a probe will help greatly in establishing an accurate relationship between the intensity required to produce a certain phenomenon and the final results so obtained.
Intensitl Measurements in the
Cylindrical Transducer

So far, not much attention has been paid to the
distribution of intensity in the medium under
insonation. Especially, in the case of ultrasonic
processing, the fluid was allowed to pass through the
insonating device (transducer) without making actual
intensity distribution measurements in it. For clean­
ing purposes or where the uniform intensity distribu­
tion is immaterial, the knowledge of intensity dis­
tribution may not be so essential. But, in cases
such as the present investigation, where a cylindrical
transducer was used for the dialysis through a tubular
cellophane membrane, it was imperative to know whether
the dialysis was being carried out under uniform
intensity from the cylindrical transducer. The inten­
sity distribution measurements were made with the
barium titanate probe at power control levels of
four, five, and six on the ultrasonic generator and
at two frequencies, namely, 22 and 420 kilocycles per
second.

The discussion of the intensity measurements in
the cylindrical transducer is presented under the
following headings: (1) cylindrical transducers, (2) intensity measurements at 22 kilocycles per second, and (3) intensity measurements at 420 kilocycles per second.

**Cylindrical Transducers.** The cylindrical transducers belong to the family of the focussing transducers. In the early stage of ultrasonic processing it was realized that the flat transducers were not very suitable for processing purposes as cavitationsal agitation could not be obtained in a large volume of the liquid. The next step was to design such transducers where focussing of the ultrasonic energy could be obtained. The bowl shaped transducer is an example of this type of transducer. Large amounts of energy could be obtained in the focussed zone but still a limited amount of the liquid could be processed through the focussed zone. The cylindrical transducer occupies the advantage of being a transducer in which long exposure to ultrasonics can be obtained at reasonable flow rates for the liquid flowing through the transducer.

Cylindrical transducers possess a line focus along the axis of the cylinder, that is, the ultrasonic waves generated from all sides of the
transducer are focused along the axis. If another cylindrical tube, such as the tubular dialyzing cell, is placed in the center of the cylindrical transducer the ultrasonic waves would strike the cell surface at uniform intensity. Such an arrangement seemed ideal for the countercurrent dialysis of caustic solutions in the presence and absence of ultrasonics. For this reason and to know whether or not a uniform intensity was being obtained on the dialyzing cell surface, the sonic field distribution of the cylindrical transducer was mapped.

**Intensity Measurements at 22 Kilocycles per Second.** Intensity measurements were made at the power control levels of four, five, and six on the ultrasonic generator. The results obtained are presented in the following manner: (1) horizontal distribution at various depths, and (2) vertical representation of intensity distribution.

**Horizontal Distribution at Various Depths.** As was expected, the intensity values increased with increasing power control levels on the ultrasonic generator. This can be seen from Table V, page 115, where intensity values at
various depths and positions are tabulated. For example, for the diameter AA at a depth of one
inch the intensity values at five measured positions were: 0.061, 0.056, 0.056, 0.056, and
0.063 volts at power level four; 0.076, 0.072,
0.070, 0.072, and 0.078 at power level five;
and 0.079, 0.084, 0.074, 0.075, and 0.089 at
power level six. This increase in the intensity
values with the increase in power control levels
is obvious, as the intensity of vibration produced
by the generator increases as the power control
level is increased. Therefore, the values
measured by the probe at corresponding power
levels would also increase. However, the interest­
ing part to examine is the values of intensity at
various depths.

Vertical Representation of Intensity Distr­
bution. The results obtained for the vertical
representation of intensity distribution are dis­
cussed under the following headings: (1) inten­
sity distribution at the transducer, (2) inten­
sity distribution at the intermediate position
(also called at the membrane position),
(3) distribution at the center, and (4) intensity distribution ranges at the above three positions.

**Intensity Distribution at the Transducer.**

Results on the intensity distribution at the transducer are presented in Figures 25, 26, and 27, pages 122, 123, and 124. It is observed that the intensities at depths of one, two, and three inches from the top of the transducer are smaller than the values at the bottom three inches. From Table V, page 115, at power dial four, the intensity at the transducer at positions 12.00, 3.00, 6.00, and 9.00 based on clock analogy are: 0.068, 0.076, 0.066, and 0.072 at one inch depth; 0.092, 0.092, 0.091, and 0.091 at two inch depth; 0.099, 0.095, 0.096, and 0.099 at three inch depth; 0.099, 0.097, 0.099, and 0.092 at four inch depth; 0.099, 0.096, 0.095, and 0.098 at five inch depth; and 0.100, 0.100, 0.100, and 0.099 at six inch depth. As a matter of fact, the intensity values still increase but not to the extent as
they increased from the first two inches to the depth at three inches. This point can be seen clearly from the curves of Figure 26, page 123. There is a sudden increase in the intensity value from first to the second point from the top, and after that the increase in value is gradual.

The sudden jump in the intensity value from the first two positions to the third may be explained as follows. The actual transducer, that is, the barium titanate element, is only the bottom five inches of the soni-cell out of a total length of seven inches of the soni-cell. The remaining two inches at the top is copper cylinder of the same diameter as the element. It appears that the two inch copper section at the top also vibrates, though somewhat weakly as compared to the element, in consonance with the actual element (transducer).

A regular trend is observed of the intensity values increasing from the top of the transducer to the bottom. This
fact is amply borne out by Figure 26, page 123, wherein the depth is plotted as the ordinate and the intensity as the abscissa.

Another fact which comes to light is the unequal distribution of intensity from one side of the transducer to the other side, as shown in Figure 21, page 118. For example, it is found that, in general, the intensity values in the region between the positions 12.00 to 6.00, based on clock analogy, are greater than on the side in the region from 7.30 to 10.30. Examining the data at the depth of two inches the intensity values at the right hand three positions from the top are 0.099, 0.100, and 0.100. Whereas, the corresponding values on the left hand side are 0.097, 0.097, and 0.097. This may not be true in all cases but a definite trend is visible from Figure 21, page 118. It can be said, therefore, that the values of intensity on the right hand side, that is, between the positions 12.00 and 6.00, are somewhat
larger than for the corresponding values on the left hand side.

This discussion brings out the points that intensity at the transducer is not only non-uniform depthwise, but it also varies at different positions of the transducer.

**Intensity Distribution at the Intermediate Position.** Results for the intensity distribution at the intermediate position (at the membrane) are shown in Figures 31, 32, and 33, pages 128, 129, and 130, respectively. The physical appearance of the curves in this case is similar to the curves obtained at the transducer.

It is found that the intensity values in this case are greater, except at the depths of one and two inches, than the corresponding values obtained at the transducer. This holds true for all of the three power control levels. For example, at positions 12.00, 3.00, 6.00, and 9.00, and at power level five, the intensity values at the membrane are: 0.080, 0.081, 0.073, and 0.083 at the
depth of one inch, 0.094, 0.092, 0.092, and 0.093 at the depth of two inches. The corresponding intensity values at the transducer were: 0.087, 0.086, 0.080, and 0.088 at the depth of one inch, and 0.096, 0.090, 0.095, and 0.094 at the depth of two inches. For the remaining depths, namely, three, four, five, and six inches it is found that the intensity values at the membrane position are always greater than those at the transducer. This can be seen from the values shown in Figures 19, 20, and 20, pages 116, 117, and 118, respectively.

The difference in vibrational behavior between the top two-inch portion and the bottom five-inch portion of the cylindrical transducer is probably due to the method of construction of the soni-cell. As has been stated earlier, out of the total length of seven inches only the bottom five inches comprise the actual element. The rest of it is copper cylinder. Therefore, in the case of the top two-inch portion the
intensity would decrease as the distance increases away from the transducer. However, for the bottom five inches, the intensity would increase as the distance increases away from the transducer as the axial focus is being reached. In this case, that is, at 22 kilocycles per second, the question of absorption does not seem to affect the intensity.

**Intensity Distribution in the Center.**

Intensity data for this position are presented in Figures 37, 38, and 39, pages 134, 135, and 136, respectively.

In the light of the hypothesis advanced in the previous case, it is expected that for the top two-inch portion the intensity values should be lower than the values at the intermediate position, and for the remaining four-inch portion the intensity values should be higher at the center than at the intermediate position. Figures 19, 20, and 21, pages 116, 117, and 118, respectively, show clearly that the hypothesis holds in this case also.
Intensity Distribution Ranges at Various Depths. The intensity distribution ranges for power control levels four, five, and six are shown in Figures 43, 44, and 45, pages 140, 141, and 142, respectively.

These curves were plotted to see the general shape of the intensity versus depth relationship at the transducer, at the intermediate position, and at the center. The curves shown in Figures 43, 44, and 45, pages 140, 141, and 142, respectively, indicate that the increase in intensity is rapid for the top two inches of the transducer and then there is a gradual increase in the intensity values with depth.

Intensity Measurements at 420 Kilocycles per Second. Intensity measurements at this frequency are somewhat different than those at the lower frequency of 22 kilocycles per second. The horizontal distribution of the intensity at various depths of one, two, three, four, five, and six inches has been represented in exactly the same way as that in the case of low frequency. Intensity measurements are to some extent
complicated by the modes of vibration of the focussing cylinder.

It is known that there are three possible fundamental modes of vibration in a cylindrical transducer\(^{(171)}\). They are: (1) the length mode of vibration in which the fundamental resonance frequency is determined essentially by the length of the cylinder, the vibrating tube becomes longer and shorter; (2) radial mode, its fundamental resonance frequency is determined essentially by the tube diameter, the vibrating tube becomes larger and smaller in diameter; and (3) wall-thickness mode of vibration in which the fundamental resonance is determined essentially by the wall thickness, and the vibrating wall becomes thicker and thinner.

A diffraction-type line focus can be generated at the cylinder axis only by excitation of the thickness mode of vibration. At frequencies below 100 kilocycles per second the cylinder dimensions required for this mode of vibration become impracticable. The preferred mode of vibration in this frequency range is the radial mode.
So, whereas at the lower frequency of 22 kilocycles per second the preferred mode of vibration is radial, at the higher frequency it changes to thickness mode of vibration or probably a combination of radial and wall-thickness mode of vibration. This change in the mode of vibration would have some effect on the measurements of intensity at the higher frequency of 420 kilocycles per second.

It is found that the range of intensity values at 22 kilocycles per second is different from the range at 420 kilocycles per second. For example, the intensity range for 22 kilocycles per second is from 0.05 to 0.12 volts, whereas that for 420 kilocycles per second is from 0.4 to 1.4, almost ten times as much.

It is considered that this ten fold increase in the intensity values is due to the increase in the frequency and therefore change in the mode of vibration. The increase in frequency would also affect
the intensity in the following manner. Intensity is given by the formula:

\[ I = 2 \pi \rho N^2 A^2 v \]  \hspace{1cm} (13)

where:

- \( I \) = intensity in ergs/cm\(^2\)
- \( \rho \) = density of the medium, gm/cm\(^3\)
- \( A \) = amplitude of vibration, cm
- \( N \) = frequency of vibration, sec\(^{-1}\)
- \( v \) = velocity of sound in the medium, cm/sec

If, on the right hand side of this equation, all the factors remain constant except the frequency, it is seen that the intensity increases proportionally as the square of the frequency.

The results obtained in the intensity measurements at 420 kilocycles per second are discussed under the following headings: (1) distribution at the transducer, (2) distribution at the intermediate position, (3) distribution at the center, and (4) distribution ranges of intensities at these three positions.
Intensity Distribution at the Transducer.

It is seen that the curves obtained for the intensity distribution at various depths at the transducer, at power control levels four, five, and six are different from those obtained at the same positions at 22 kilocycles per second (see Figures 28, 29, and 30, pages 125, 126, and 127, respectively). Especially, the curves at the positions from 3.00 to 7.30 at power levels four and five, show a large bulge in the middle. Whereas, the curves at 22 kilocycles per second show no such bulge. Also, curves in Figures 28 and 29, pages 125 and 126, respectively at positions 12.00 and 1.30 are similar to those at 9.00 and 10.30. This indicates, as was pointed out in the case of 22 kilocycles per second, that the intensity values are not uniform on all sides. If the figures representing the data horizontally, Figures 22, 23, and 24, pages 119, 120, and 121, respectively, are seen it would mean that the intensity of vibrations on the right hand side are different from that on the left hand side. It appears that these changes are due to the high frequency
of vibration. As has been stated earlier, at lower frequency the mode of vibration of the cylindrical transducer is radial and at 420 kilocycles per second it probably becomes complicated by the wall-thickness mode of vibration. Also, the absorption of sound, being proportional inversely to the square of frequency, increases greatly. How much these factors affect to produce the type of curves as are shown in Figure 28, page 125, and Figure 29, page 126, is not understood clearly. As the transducer is five inches long from the bottom, the intensities at the bottom portion would be more intense as compared to that at the top two inches. That probably is the reason that the intensity values at the top two inches are lower than the values at three, four, five, and six inch depths.

However, the curves for intensity measurements at power control level six are different from those obtained at power control levels four and five. The curves obtained at the transducer for power control level six, Figure 30, page 127, do not show any bulges in the middle. The
curves are more or less straight lines. Probably, this difference in behavior is on account of greater power at power level six than at four and five. It appears, at power level six, sufficient power is supplied to the transducer that the top two inches of it vibrates more strongly than it vibrated at power control levels four and five.

It would appear that for a certain transducer and at a certain frequency the shape of the intensity-depth curves should remain the same, if only the power control levels on the transducer are varied. The only change produced should be in the values of intensity which would increase as the power control level increases. However, the results obtained above do not conform to this hypothesis, as the intensity-depth curves at power control level six are different than those at power control levels four and five. This change in the shape of intensity-depth curves with increase in intensity and also with change in frequency, would have a great bearing on the processes being
carried out in the presence of ultrasonics. Especially, for an investigation such as the present one, it would mean that there was greater insonation at the center of the dialyzing cell (at 420 kilocycles per second) than it was at the top or bottom.

**Intensity Distribution at Various Depths at the Intermediate Position.** When intensities at the intermediate position (or at the membrane) are observed, it is found that they are generally smaller than the corresponding values at the transducer (see Figures 22, 23, and 24, pages 119, 120, and 121, respectively). For example, in Figure 23, page 120, at power control level five and at a depth of four inches, the intensity values at the intermediate position are 1.1, 1.1, 1.05, 1.05, 1.05, 1.0, 1.0, and 1.05 volts. The corresponding values at the transducer are 1.12, 1.2, 1.2, 1.3, 1.3, 1.2, 1.1, and 1.1 volts. The decrease in the intensity values at the intermediate position may be on account of two reasons. Firstly, it may be due to the absorption of ultrasonics.
The greater the point of measurement away from the source of ultrasonics, the smaller the intensity would be. Secondly, it may be on account of cavitation in the medium; if the intensity is such that cavitation is produced in the medium being insonated, as was the case, that will also lessen the intensity with increasing distance.

Theoretically, the intensity from all of the points on the transducer should converge into a line focus along the axis of the cylinder; this means that the intensity should be maximum at the center of the transducer. Intensity should increase as one moves towards the center. However, the data show that the intensity values at the intermediate position are smaller than those at the transducer which is contrary to what is predicted by the theory. The decrease in the intensity values at the intermediate position is, probably, on account of cavitation which absorbs the ultrasonic energy greatly.

These observations show that for those investigations where the effect of intensity
is required to be studied, such as in the case of dialysis where the intensity should be uniform over the surface of the dialyzing cell, a probe is essential to map the intensity at various points.

**Intensity Distribution at Various Depths at the Center of the Transducer.** Figures 40, 41, and 42, pages 137, 138, and 139, respectively, show the graphs for the intensity distribution at the center of the transducer. It is seen that all the curves at three power control levels four, five, and six possess almost the same shape. Also, the curves are much more smooth than those obtained at the transducer and at the intermediate position. Values of intensity increase at the center from the power control level four to six as would have been expected. This is seen from Figures 22, 23, and 24, pages 119, 120, and 121, respectively.

**Intensity Distribution Ranges at Various Depths.** The intensity distribution ranges at various depths and for power control levels four, five, and six are shown in Figures 46,
47, and 48, pages 143, 144, and 145, respectively. The intensity values were plotted in this manner to learn the shape of the curves at the three positions, namely, at the transducer, at the intermediate position, and at the center. These curves show that the intensity increases in all the three cases from top to the bottom. More sonic intensity is obtained from the bottom part of the transducer than from the top part of it. If a phenomenon is studied where the question of boundaries is involved this would mean that the disturbance produced at the top would be less than at the bottom, and would increase gradually as the bottom is reached.
Intensity measurements in this case were made only at 420 kilocycles per second. The same RICH-ROTH type "400" ultrasonic generator was used in this case also. Only one frequency was used because the transducer was designed to be used only at this frequency. Intensity measurements were made at three power control levels, namely, four, five, and six, the same as in the case of the intensity measurements in the soni-cell.

The results obtained are discussed under the following headings: (1) theoretical considerations in the vibration of a bowl shaped transducer, and (2) shape of the curves.

Theoretical Considerations. Theoretical considerations show that in any type of focusing device the sharpness of the focal point is proportional to the ratio of the aperture of the device to the wave-length. In Figure 61, page 201, is shown the pressure distribution on the axis of a bowl shaped transducer. For this transducer, the ratio of the aperture to the wave-length is equal to eight, and the angle of convergence is equal to 90 degrees. In Figure 61, page 201, the
Figure 61. Axial Pressure Distribution for a Bowl Shaped Transducer

ordinate is \( p/p_0 \) and the abscissa is \( z/\lambda \) (\( p_0 \) is the pressure at the transducer face, \( z \) the axial distance from the face of the transducer, and \( R \) the radius of curvature). At the focus (\( z/\lambda = 11.3 \)) the peak sound pressure is about twenty times greater than the average sound pressure at the surface of the transducer.

Several interference maxima and minima occur along the axis as is seen from Figure 61, page 201. The axial pressure distribution for a transducer bowl shows a main lobe surrounded by several side lobes. However, the main lobe carries about 84 per cent of the total energy radiated by the transducer.

In the focal plane the radius of the circular cross section of the main lobe is determined by the relation (171):

\[
   r_F = 0.61 \times R \lambda / a
\]  

(14)

where:

\( r_F \) = radius of the main lobe, cm
\( R \) = radius of curvature of the transducer, cm
\( \lambda \) = wave-length of sound, cm
\( a \) = aperture of the bowl shaped transducer, cm
If the total power output of the transducer is \( W \), the average intensity of the main lobe in the focal plane is given by the relation:

\[
I_F = 0.84 \times \frac{W}{\pi r_F^2} = 0.71 \times W \left(\frac{a}{\lambda R}\right)^2 \quad (15)
\]

where:

- \( I_F \) = average intensity of the main lobe, \( \text{watts/cm}^2 \)
- \( W \) = total power output of the transducer, \( \text{watts} \)

The power \( W \) is related to the effective intensity by the relation:

\[
W = I_o \times S_o \quad (16)
\]

where:

- \( W \) = total power output of the transducer, \( \text{watts} \)
- \( I_o \) = effective intensity at the transducer face, \( \text{watts/cm}^2 \)
- \( S_o \) = total radiating area of the transducer, \( \text{cm}^2 \)
But

\[ S_0 = 2 \pi R^2 \left( 1 - \cos \frac{\alpha}{2} \right) \]  \hfill (17)

where:

\[ \alpha = \text{the angle of convergence, degrees} \]

Thus, equation (16) can be expressed as

\[ \frac{I_F}{I_0} = 1.42 \left( 1 - \cos \frac{\alpha}{2} \right) \left( \frac{a}{\lambda} \right)^2 \]  \hfill (18)

The peak pressure gain is given by the relation:

\[ \Gamma_g = 2.2 \left( \frac{I_F}{I_0} \right)^{\frac{1}{2}} \]  \hfill (19)

where:

\[ \Gamma_g = \text{peak pressure gain in the focussing bowl, dimensionless} \]

Here, the factor 2.2 relates average pressure to peak pressure at the center of the focal area. For a 90 degree bowl shaped transducer

\[ \Gamma_g = 2.6 \left( \frac{a}{\lambda} \right) \cong 1.8 \left( \frac{R}{\lambda} \right) \]  \hfill (20)
In the case of the transducer used in this investigation, radius of curvature \( R = 6.3 \) centimeters, and aperture is equal to 4.5 centimeters. Therefore, the pressure gain at a frequency of 400 kilocycles per second is:

\[
\Gamma_g = 1.8 \left( \frac{R}{\lambda} \right)
\]

\[
= 1.8 \left( \frac{6.3}{1500 \times 100 \over 400 \times 1000} \right)
\]

\[
\approx 31
\]

If an intensity of two watts per square centimeter is assumed to be at the transducer face, the theoretical peak focal intensity would be:

\[
I_{\text{peak}} = I_0 \times \Gamma_g^2 \quad (\Gamma_g = 31)
\]

\[
= 2 \times 961
\]

\[
\approx 2000 \text{ watts/cm}^2
\]

which shows that though the intensity at the transducer face is as low as two watts per square centimeter, yet at the focus peak intensity it is one thousand times as much.
Shape of the Curves. The data are presented in graphical form in Figures 52, 53, and 54, pages 150, 151, and 152, respectively. Here, the abscissa represents the positions at which the measurements were made and the ordinate represents the intensity values in volts. The six curves at each diameter are at depths of 1/2, 1, 1-1/2, 2, 2-1/2, and 3 inches from the top of the liquid. The number adjacent to the curve indicates the depth at which measurements were made.

It is seen from these graphs that the intensity curves for 1/2 and 1 inch levels show a slight peak in the middle. The peak in the middle indicates that the intensity at this point is greater than at other points for the same depth. However, when the curves corresponding to the remaining depths, namely, 1-1/2, 2, 2-1/2, and 3 inches, are examined, it is found that they show a dip in the middle instead of a peak. This phenomenon is shown by all of the curves at all of the four diameters and at all of the three power control levels.

According to theoretical considerations the value of intensity at the focus should be almost one
thousand times the intensity at the face of the transducer. The observations show that the intensity values were larger at the periphery of the bowl shaped transducer than at any point along its axis. For example, for power levels four, five, and six, at the depth of two inches and along the diameter BB, the intensity values at the center were 0.79, 1.5, and 1.9, and the corresponding values at the periphery were 0.98, 2.1, and 2.3, respectively.

This disparity between the theoretical and experimental results brings up the necessity to map the sonic field of a transducer before it is used for some operation. It is possible that the low intensity value, obtained at the center, may be on account of ultrasonically produced cavitation. Cavitation would absorb the ultrasonic energy and the values of intensity obtained in the medium would be less.

Another interesting feature of the curves appears to be that whereas the curves for 1/2 and 1 inch are close together there is a big jump in intensity values when the curve corresponding to the depth of 1-1/2 inches is examined. (See Figures 52, 53, and 54, pages 150, 151, and 152, respectively.) Also, the
transition from a peak in the middle to the dip in the middle takes place in this region. It appears that ultrasonic energy does not reach up to the top of the liquid surface directly. As the transducer is a spherical segment, the ultrasonic waves would arrive at a focus along the axis. From the observations it seems that the focus would lie somewhere between 1 and 1-1/2 inches from the top of the liquid and the transition takes place starting from the focus. In the upper one inch part of the liquid the pressure detected would then be due to diffracted and stray ultrasonic waves.

If the values of intensities are compared for the cylindrical and bowl shaped transducers it is found that the range of values is much larger for the bowl shaped transducer than it is for the cylindrical transducer. For example, the range for the bowl shaped transducer is from 0.5 to 2.9 volts, whereas for the cylindrical transducer it is from 0.4 to 1.4 volts. No theoretical comparison of the two transducers could be made as they have different geometrical shapes.
Soni-Dialysis of the Caustic Solution

Soni-dialysis of 0.24 N caustic solution involves the discussion of the following points: (1) development of the dialyzing cell, (2) attainment of equilibrium during insonation, (3) sono-dialysis of the caustic solution, (4) feasibility of the application of Fick's law, and (5) effect of flow rates on sono-dialysis.

Development of the Dialyzing Cell. The problem of the development of the dialyzing cell is discussed under the following headings: (1) behavior of the dialyzing cell under dialysis, (2) smoothness of the dialyzing cell surface, and (3) behavior of the cell in the presence of ultrasonics.

Behavior of the Dialyzing Cell under Dialysis. It was found that reproducible results could not be obtained when dialysis constant was calculated from the counter-current dialysis in the absence of ultrasonics. A search of the literature showed that cellophane swells in water or caustic solution and its porosity increases (95, 96, 172). The porosity of the membrane swollen in caustic depends upon
both the temperature and concentration. In general, an optimum concentration exists for each temperature, the optimum being more pronounced and swelling greater at low than at higher temperatures. McBain and coworkers (95) have reported that all the increase in porosity and thickness of cellophane takes place in the first 15 to 20 minutes of contact with caustic. Further treatment with caustic does not increase the pore size.

It is considered that the non-reproducibility of results was on account of the pretreatment effect mentioned above. After the cellophane was treated with caustic for one-half hour, reproducible results were obtained in the dialysis without ultrasonics. For this reason, in all later experiments dialyzing cell was always pretreated with 0.24 N caustic solution at 23 to 24 °C before a test was made.

Storage of the membrane was another important item. It is known that cellophane tends to dry when stored under atmospheric conditions on account of evaporation of moisture. As the cellophane dries, its mechanical strength
decreases. Therefore, to keep the cellophane saturated with water vapor so that it does not lose its mechanical strength, it was stored over water. A desiccator, half filled with water was used as the storage place.

**Smoothness of the Dialyzing Cell Surface.**

In the early phase of this investigation the bottom of the dialyzing cell was closed with a nylon thread. This left the bottom portion of the cell somewhat crimped. Sharp corners were visible at the bottom portion. This type of arrangement served well as long as the cell was not placed in the field of ultrasonics. However, when the cell was placed in the sonic field, it began to leak, usually within 20 to 30 minutes. It was observed that in most cases the leaks developed at the bottom portion of the cell. After trying various methods to obtain a smooth crimp-free bottom portion, a rubber stopper was found to be most suitable to close the bottom part of the cell. This arrangement stopped the leaks which were being produced at the bottom portion in the presence of ultrasonics.
Behavior of the Dialyzing Cell under Insonation. When the dialyzing cell was placed in the field of ultrasonics, leaks started appearing again. In this case, however, the leaks appeared at the middle portion of the cell instead of at the bottom. The time during which these leaks were produced did not show any regular pattern. The time varied from as low as ten minutes to about two and one-half hours after the cell had been placed in the soni-cell and exposed to ultrasonics. Sometimes the leaks were very tiny holes, just pinholes, and sometimes they were almost as large as one millimeter. There was no regular pattern in which the leaks were produced. This suggests that the cellophane membrane (thickness = 0.001 inch) is not uniform. The leaks appear wherever a non-uniformity (or weakness) exists in the structure of the membrane.

As the ultrasonics exert alternating high pressures and impart high accelerations to the particles of the medium being insonated, it will
have the same effect on the cellophane molecules also. The consistent alternating pressures and accelerations may dislocate the cellophane molecules, and as an ultimate result rupture of the membrane may take place. The rupture would probably occur at the weakest place (or point) in the membrane.

It is known that treatment with caustic increases the pore size of the cellophane membrane and produces swelling. The membrane may not return to its initial porosity even when cleaned and allowed to dry. For this reason, a new, treated membrane (or a new dialyzing cell) was used with each experiment.

**Attainment of Equilibrium during Insonation.**
According to the countercurrent operation theory, the system under consideration would come to equilibrium at a certain point after some time. In the present investigation of the study of countercurrent dialysis of caustic solution with water, equilibrium was attained in about two hours in the absence of ultrasonics. However, when ultrasonics was used it was found that leaks were produced in the membrane and
it could not be predicted at the start of the experiment at what time the leak may occur. The solution was found in plotting the reciprocal of time against the reciprocal of the titer value of raffinate or extract, whichever was in question. A straight line relationship was found to hold in these two cases. For example, to find the equilibrium value of the extract, the reciprocal of time was plotted against the reciprocal of titer value, and a straight line was thus obtained. The titer value corresponding to time equal to two hours was read from the graph. These values (equilibrium values) were used in the calculation of the overall mass transfer coefficients (dialysis constants) and are shown in Table X, page 164.

The equilibrium values of extract and raffinate obtained by this extrapolation method require only three points, that is, only three titer values corresponding to three time values. The method, therefore, eliminates all of the guesswork, and saves time.

It is not known why a straight line relationship should exist between the reciprocals of the titer value and time. However, the actual plots show that
such a relationship does exist. It would appear, therefore, that in a countercurrent operation or in any operation where the quantity desired (such as the equilibrium value in this case) reaches an equilibrium with time, if reciprocals are plotted (such as in the present investigation) a straight line relationship would exist.

**Sono-Dialysis of a 0.24 N Caustic Solution.** The following factors appear to control the dialysis in the presence of ultrasonics: (1) effect of ultrasonics on dialysis, (2) temperature rise on account of ultrasonic absorption, and (3) intensity of ultrasonics and its distribution on the membrane.

**Effect of Ultrasonics on Dialysis.** It is not understood how ultrasonics effects the dialysis. The work in this field has been almost negligible. There are not enough data at present to formulate more than a hypothesis.

In mass transfer operations, it is generally assumed that mass transfer occurs according to the concepts of the two-film theory and that the mass transfer takes place through various resistances at the phase boundary. In this particular case, for caustic to diffuse through the membrane
it has to pass three resistances, namely, the caustic film on one side of the membrane, the membrane itself, and the water film on the other side of the membrane.

When ultrasonic waves strike the membrane they produce agitation on the surface of the membrane and disturb the film on the water side of the membrane. Similarly, the film on the caustic side of the membrane would also be disturbed and agitated by ultrasonics as it easily passes through the cellophane membrane.

As ultrasonic waves pass through a medium they produce alternating high and low pressures in the medium. In other words, a given point in the medium is subjected to rapidly alternating compression and tension. It is conceivable, therefore, that these alternating compressions and tensions would tend to disturb the static liquid films on either side of the membrane. This agitation and partial or total removal of the liquid films would tend to increase the rate of mass transfer. As the intensity is increased,
first the dialysis constant would tend to increase but after a certain value of intensity has been reached further increase in intensity would not show much effect. This is quite possible as at some intensity films on both sides of the membrane may disappear completely, and any further increase in mass transfer may not take place.

Temperature Rise. During dialysis, in the presence of ultrasonics, the temperature of the fluids in the soni-cell and dialyzing cell rose from room temperature to a temperature dependent on the intensity of insonation. For example, for the intensity corresponding to power control value two, the temperature arose from 22 to 32 °C in 20 minutes, whereas for the intensity corresponding to power control value six, the corresponding rise was from 22.5 to 45.4 °C. (See Table VII, page 153.) It is known that dialysis constant is dependent on temperature and increases with increase in temperature.

It is seen from Table VII, page 153, that the rate of temperature rise was different at different intensities, that is, the rate of
increase of dialysis constant with temperature would also, then, vary. In other words, at different intensities, besides the ultrasonic intensity, another variable appears, namely, the variable of dialysis constant with temperature. Therefore, under the present circumstances, it does not appear that the dialysis constants can be compared at various intensities because the additional effect of temperature complicates the picture.

Intensity of Ultrasonics and its Distribution on the Membrane. It has been discussed earlier what type of intensity distribution is obtained in a soni-cell. Sono-dialysis experiments were conducted in the same soni-cell. According to the earlier findings the intensity striking the dialyzing cell (that is, the membrane) is not uniform. The intensity increases from top to bottom, or in other words, the top two to three inch portion of the dialyzing membrane is exposed to less disturbance due to ultrasonics than the bottom portion. In this case, therefore, it will be more appropriate
to consider the dialysis constant as the average overall mass transfer coefficient rather than the dialysis constant in the strict sense.

**Feasibility of Application of Fick's Law.** Fick's law is based on the assumption that the concentration gradient \( \frac{dc}{dx} \) is uniform at all of the points equidistant from the membrane. It has been mentioned earlier that under insonation, the intensity is not uniform at a surface at some distance from the soncell. The intensity would be smaller at the top portion of the surface and greater at the bottom portion. This means that the concentration gradient would be different at the top portion than at the bottom.

If the concentration gradient is not uniform around the membrane (dialyzing cell) it would seem that the usual Fourier type equation, employed to calculate the mass transfer coefficients, could not be used in this case. Probably, this may be one of the reasons that no smooth trend can be obtained when intensity values are plotted against the overall mass transfer coefficients in Figure 55, page 155. Another reason may be the different rate of temperature rise as has been reported earlier.
It is pointed out here that the non-uniformity of the concentration gradient along the surface of the dialyzing cell would not have been thought of if the intensity measurements had not been made with the probe. In investigations such as the present one, it is always advantageous to map the sonic distribution of the transducer to learn what type of intensity distribution exists. This is essential as it has been found that the actual intensity distribution differs in many cases from that assumed on a theoretical basis.

**Effect of Flow Rates.** It is considered that the flow rates of five milliliters per minute for caustic solution and eleven milliliters for water, used in this investigation, were low. Flow rates for both caustic and water should be increased. Considering the inside of the dialyzing cell, at the present flow rate of five milliliters per minute for caustic the chances of its coming in contact with the membrane for diffusion will be small. In other words, the probability that all of the molecules of sodium hydroxide which are introduced into the dialyzing cell will have an equal chance of diffusion through
the membrane, is very small. It cannot be said how much of the solute introduced actually comes into contact with the membrane. The same thing can be said for water. This fact would introduce error in the calculation of the equilibrium values of extract and raffinate which in their turn would introduce error into the calculation of the overall mass transfer coefficient. Its effect can also be seen in the material balance for caustic as shown in Table XI, page 172. It is found that total caustic in, is not equal to material out, in any case.

It is suggested, therefore, that a dialysis test be conducted with dyed caustic solution without placing the dialyzing cell in the soni-cell. Since the dialyzing cell is transparent the dispersion of the dyed caustic solution in the dialyzing cell would show how much of the caustic solution comes into contact with the membrane.
Recommendations

Recommendations arising from the mapping of intensity distribution in the soni-cell and bowl shaped transducers, and the determination of the overall mass transfer coefficients in the counter-current dialysis of 0.24 N caustic solution in the presence and absence of ultrasonics are presented below.

Barium Titanate Probe. The hypodermic needle carrying the barium titanate tip should be joined to a thin tubing as a holder instead of 1/2-inch lucite rod. The suggested measurements of the tubing are: diameter = 1/8-inch, and length = eight inches. This would decrease the bulk of the probe and also make it easier to explore the field by increasing its operational flexibility.

Calibration of the Probe. The probe should be sent to an ultrasonic equipment manufacturer so that it can be calibrated. The manufacturers recommended are: Brush Electronics Company, and the Massa Laboratories.

Arrangement for Holding the Probe. The arrangement shown in Figure 17, page 103, for holding the
probe to measure the intensity distribution should be improved so that greater accuracy can be obtained in the movements of the probe depthwise and horizontal-

**Thickness of the Membrane.** A cellophane membrane of greater thickness than that used in the present investigation should be tried. Leaks were easily produced in the membrane used in the present investigation (thickness = 0.001 inch), when it was placed in the field of ultrasonics. It is suggested that cellophane tubing of a thickness of about 0.002 to 0.003 inch be tried.

**Larger Flow Rates.** Larger flow rates than those used in this investigation should be tried. It is recommended that a flow rate of about 10 to 20 milliliters per minute for caustic and about 30 to 40 milliliters per minute for water be used to allow a better contact of caustic solution and water with the membrane than with the present flow rates.

**Manifold in the Dialyzing Cell.** A manifold should be connected at the end of the caustic inlet inside the dialyzing cell so that the liquid passing through the cell can be dispersed and has a greater
possibility of coming into contact with the membrane than in the present case.

**Interchange of Water and Caustic.** Instead of the caustic being in the dialyzing cell and water in the soni-cell, water should be allowed to flow through the dialyzing cell and caustic in the soni-cell. That is, water and caustic should be interchanged in the dialysis arrangement so as to provide a better contact with the membrane on account of direct micro-agitation action of ultrasonics.

**Temperature Coefficient of Dialysis.** It is recommended that temperature coefficient of dialysis should be determined. In this investigation, the temperature arose from 23 to 49 °C when dialysis was performed in the presence of ultrasonics. As it is not known how much increase in dialysis constant is due to temperature, temperature coefficient determination will indicate the effect of temperature on dialysis constant, and it will be possible to determine the net effect of ultrasonics on the dialysis constant.
Limitations

Limitations on the mapping of intensity distribution in cylindrical and bowl shaped transducers, and the determination of overall mass transfer coefficients in the sono-dialysis of 0.24 N caustic solution with water, are presented in this section.

**Barium Titanate Probe.** The barium titanate probe was designed and constructed to map the intensity distribution in sonic fields. A small cylindrical barium titanate transducer, 1/16 inch diameter and 1/16 inch in length, was used as the detector-converter element. The element was mounted in a hypodermic needle, three inches long, which in turn was mounted in a lucite rod, 1/2 inch diameter and five inches long. The alternating voltages generated by the element were measured by a vacuum tube voltmeter.

**Ultrasonic Equipment.** A RICH-ROTH type "400" ultrasonic generator was employed in this investigation. A cylindrical transducer (soni-cell) connected with the generator was used as the source of insonation in the sono-dialysis experiments.

**Evaluation of the Probe.** Soni-cell, type L-250, and the bowl shaped transducer were employed to
evaluate the barium titanate probe. In both cases intensities were measured in distilled water. In the case of the soni-cell, frequencies used were 22 and 420 kilocycles per second and power control levels four, five, and six on the ultrasonic generator. For the bowl shaped transducer the frequency used was 420 kilocycles per second at the same power control settings on the generator.

System for Sono-Dialysis. Caustic solution of 0.24 N strength was used as the inner liquid in the determination of the overall mass transfer coefficients. Sono-dialysis was carried out in the soni-cell at a frequency of 22 kilocycles per second, and at power control levels of two, three, four, five, and six on the ultrasonic generator. Output impedance of the generator was at the position D.

Dialyzing Cell. Cylindrical cellophane tubing, 0.001 inch thick, 1-1/8 inch in diameter, and with an average pore diameter of 48 Ångstroms was used as the membrane in the construction of the dialyzing cell. The usable length of the dialyzing cell, that is, the length through which the mass transfer took place, was six inches.
Temperature. All sono-dialysis experiments were started at a temperature of 23 ± 1 °C. However, during insonation temperatures of the fluids in the soni-cell and the dialyzing cell rose as high as 49 °C. The temperature rise was different with different intensity. Cooling water was allowed to flow around the soni-cell at a rate of 250 milliliters per minute. This flow rate was maintained the same in all of the sono-dialysis experiments.

Flow Rates. Flow rates of five milliliters per minute for caustic and 11 milliliters per minute for water were used in the sono-dialysis experiments.
The mapping of the intensity distribution in a cylindrical transducer (soni-cell, type L-250), 2-1/2 inches in diameter and 7-1/4 inches in length, was performed at 22 and 420 kilocycles per second, at depths of one, two, three, four, five, and six inches from the top of the liquid level, and at power control levels of four, five, and six on the RICH-ROTH type "400" ultrasonic generator. Intensity distribution was also mapped in a bowl shaped transducer at a frequency of 420 kilocycles per second, at power control levels of four, five, and six on the same generator, and at depths of 1/2, 1, 1-1/2, 2, 2-1/2, and 3 inches from the top of the liquid. The intensity was measured by a probe which employed a small cylindrical barium titanate transducer, 1/16 inch in diameter and 1/16 inch in length, as a detector-convertor element. The alternating voltages thus produced were indicated by a vacuum tube voltmeter. Distilled water was used as the liquid medium in which intensity measurements were made. From this study, the following conclusions were drawn.
1. The field distribution of sonic intensity is not uniform in the cylindrical transducer (or soni-cell). It is less at the top two-inch portion of the transducer and increases gradually for the remaining five-inch bottom portion.

2. Intensity values range from 0.05 to 0.12 volts at 22 kilocycles per second and from 0.5 to 1.4 volts at 420 kilocycles per second.

3. In the case of the bowl shaped transducer, the intensity at 420 kilocycles per second at power control level six, and at the depth of two inches from the top, is 2.3 volts at the periphery and 1.9 volts at the center.

In the determination of the overall mass transfer coefficients in the countercurrent dialysis of 0.24 N caustic solution with water, at 22 kilocycles per second and at power control levels two, three, four, five and six on the RICH-ROTH type "400" generator, using cellophane tubing (1-1/8 inch in diameter and 0.001 inch in thickness) as the membrane, the following conclusion was drawn.
1. The overall mass transfer coefficient was 2.29 centimeters per minute in the absence of ultrasonics, and was 4.15 centimeters per minute in the presence of ultrasonics at a power control level four.
VI. SUMMARY

In ultrasonic processing, it has been a practice to measure intensity of ultrasonics as a product of plate current and voltage as indicated on the ultrasonic generator. At low frequencies the standard equipment is available, such as the sound level meter, to measure the absolute intensity, but at higher frequencies the problem becomes complicated by the diffraction effects on account of the size of the measuring device. In this investigation an attempt has been made to construct a measuring device (called the probe) to measure intensity.

A small barium titanate cylindrical element (1/16 inch in diameter and 1/16 inch in length) was used as a detector-convertor of the sonic pressures. The alternating voltages thus produced were indicated by a vacuum tube voltmeter. This element was cemented in a hypodermic needle which in turn was held in a lucite rod (1/2 inch in diameter and five inches in length) which werved as a holder. This arrangement was used to probe the sonic fields of cylindrical and bowl shaped transducers.
In the cylindrical transducer using distilled water, intensity measurements were made at 22 and 420 kilocycles per second, at power control levels of four, five, and six on the ultrasonic generator, and at depths of one, two, three, four, five, and six inches from the top of the liquid level. A total of 20 observations were made at each depth for one power control level and for one frequency. It was found that at both the frequencies the intensity was less at the top two-inch portion of the transducer and increased gradually for the remaining five-inch portion of the transducer. The intensity values varied from 0.05 to 0.12 volts for all of the measurements at 22 kilocycles per second. For 420 kilocycles per second, it was observed that the intensity first increased with the depth, reached a maximum value at about the middle of the transducer, and then decreased again. That is, the curves for intensity versus depth showed a bulge in the middle. However, this was true only for the curves obtained at 420 kilocycles per second and at power control levels four and five. For power control level six the regular curve, showing an increase in intensity as
the depth increases, was observed. The intensity values in this case ranged between 0.4 volts to 1.4 volts, which was about ten times as much as in the case of 22 kilocycles per second.

In the case of the bowl shaped transducer the intensity measurements were made at 420 kilocycles per second, at power control levels four, five, and six on the ultrasonic generator, and at depths of 1/2, 1, 1-1/2, 2, 2-1/2, and 3 inches from the top of the liquid level. The intensity versus depth curves showed a dip in the middle which indicated that intensity was less at the center than at the periphery. The intensity values in this case ranged from 0.5 volts to 2.9 volts for all of the three power control levels.

These findings were applied in the determination of the overall mass transfer coefficients in the countercurrent dialysis of a 0.24 N caustic solution in the presence and absence of ultrasonics. The flow rates for water and caustic were eleven and five milliliters per minute, respectively. Dialyzing cell was made from cellophane tubing of 1-1/8 inch diameter and 0.001 inch thickness. The useful dialyzing length of the cell was six inches. The power control levels
employed were: two, three, four, five, and six on the RICH-ROTH type "400" ultrasonic generator. All of the dialysis experiments were started at the temperature of 23 ± 1 °C. Cooling water was allowed to flow around the cylindrical transducer at a rate of 250 milliliters per minute. The overall mass transfer coefficients were calculated from the relationship:

\[ W = U \times A \times \Delta C_{lm} \]

where:

- \( W \) = weight of material passing through the membrane in unit time, gm/min
- \( A \) = area of the membrane, sq cm
- \( U \) = overall mass transfer coefficient, cm/min
- \( \Delta C_{lm} \) = logarithmic mean concentration gradient across the membrane, gm/ml

The values thus calculated were: 1.59, 3.06, 4.15, 2.66, 2.26, and 2.29 centimeters per minute corresponding to the power control levels of two, three, four, five, six, and no insonation, respectively.
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Addenda


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He immediately enrolled himself in the College of Science, Banaras Hindu University, Banaras, India. He received his B. Sc. degree, in Chemistry, Physics and Mathematics, in June 1946 and stood eighth out of a class of about 400 students. He received his M. Sc. degree, in Chemistry, in June 1948, from the same University.

The author taught Chemistry at Oel, Lakhimpur-Kheri, India, from October 1948 to July 1949, and at Dayanand Anglo Vernacular College, Ajmer, from July 1949 to January 1950. At that time he joined the National Physical Laboratory of India and worked in the division of Acoustics with Dr. S. Parthasarathy. He worked in the field of ultrasonics and chemical constitution. In September 1953, he left India for advanced studies in the United States.

In October 1953, the author entered the Department of Chemical Engineering, Virginia Polytechnic Institute, to pursue studies towards the degree of Doctor of Philosophy in Chemical Engineering. He held a research assistantship in the Virginia Engineering Experiment Station during his stay at Virginia Polytechnic Institute.
The author was born in New Delhi, India, on July 27, 1928. He received his high school education at Ramjas High School Number 5, Karol Bagh, New Delhi, and graduated in June 1942. He stood first in the school out of a graduating class of thirty-five students.
The author was elected to the membership of the American Institute of Chemical Engineers (student member), American Chemical Society, Phi Lambda Upsilon, honorary chemical society, and Cosmopolitan Club (president 1955-56), during his stay at Virginia Polytechnic Institute. He has ten publications in various scientific journals to his credit.

In April 1951 the author was married to Miss Mirmal Tara in New Delhi. He is the father of two girls, Daly and Neena.