THE EFFECT OF ULTRASONIC VIBRATIONS ON DIFFUSION

BY

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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July 20, 1948

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Dear Sir:

The thesis entitled "The Effect of Ultrasonic Vibrations on Dialysis" is hereby submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Respectfully submitted,

/JOHN H. REES

JHR/aw
Enclosure
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SUMMARY

Diffusion of a solute across a membrane is usually much too slow to deserve serious consideration as an operational method if some other mechanism to effect separation is available. There are times, though, when diffusion processes must be used to achieve the desired product. These include the tanning of leather, the impregnation of heavy fabrics, and dyeing. Thermodynamic theory indicates the high efficiency of diffusion in the separation of solutions. Dialysis, defined as the separation of crystalloids and colloids in solution by means of their unequal diffusion through certain membranes, is theoretically the best method to recover a low concentration solute.

The extremely slow rate of diffusion processes, however, is a serious objection to their commercial application. Very large equipment is needed to obtain sufficient output. In addition, dialysis poses the problem of suitable membranes.

The object of this thesis has been to use sonic and ultrasonic waves to increase the rates of capillary and molecular diffusion to a point where diffusion processes could economically be used in separations in place of distillation and adsorption. The ultrasonic vibrations were generated by a nickel, magnetostriction tube activated by a vacuum tube controlled, oscillating, electrical circuit.
These vibrations were applied in a dialysis cell in which a Cellophane membrane separated a solution of sodium hydroxide from pure water. The rate of dialysis was measured by noting the change of concentration of the sodium hydroxide solution at definite time intervals. A base point was established by several runs without sound and then the effect of ultrasonic vibrations was measured by holding all conditions constant except for variations in both the frequency and intensity of the ultrasonic waves used, these waves being so generated as to impinge directly upon the membrane. In the tests, frequency varied from 12,000 to 30,000 cycles per second while power input was raised from zero to nearly one and a half watts per square centimeter of membrane area.

The results can be listed as follows:

1. Dialysis appears to follow the conventional, concentration - gradient, diffusion equation

\[ \frac{dN}{dq} = K A \Delta X \]  
(1)

where \( \frac{dN}{dq} \) = transfer rate GM/Min.

\( K \) = membrane dialysis constant CM/Min.

\( A \) = membrane area CM²

\( \Delta X \) = concentration gradient driving force across the membrane GM/CM³

2. Increasing the power input to the oscillating unit at constant frequency from 0.0 to 1.41 watts per
square centimeter of membrane area resulted in an increase in dialysis rate. This increase was evidently due to the greater intensity of the ultrasonic vibrations at high power input. The increased rate due to greater intensity seemed to reach a plateau for all frequencies at the highest power input used (1.41 watts/CM\(^2\)). Due to limitations of the high voltage supply unit, higher power inputs could not be investigated to determine if the plateau really existed.

3. Increasing frequency at constant power input also resulted in an increase in dialysis rate. This increase continued to show progressive improvement up to the highest frequency used.

4. As noted above, the maximum improvement was obtained at maximum frequency and power input. The membrane dialysis constant \(K\) at these conditions was 0.0380 CM/Min. as against a \(K\) value of 0.0280 CM/Min. with no sound. This represents a rate of mass transfer 136% of the base rate.

Only tentative conclusions can be drawn from the above results. A 36% increase in dialysis rate at a power input of 1.4 watts/CM\(^2\) of membrane area and a frequency of 30,000 cycles/second could hardly be used to demonstrate the economic feasibility of dialysis plus ultrasonics as
opposed to distillation and adsorption. However, from the standpoint of the investigation it can be concluded that dialysis follows the classic diffusion equation and also that ultrasonic vibrations have a fundamental effect on the dialysis rate. This effect apparently is to decrease the membrane and/or liquid film resistance and thereby to increase the rate of diffusion.

While, based on the facts in this report, increased commercial applications of dialysis cannot be recommended, it is felt that further research should be encouraged. Added work could profitably be employed to investigate several fields. These include:

1. Separating the fundamental variables influencing dialysis and defining their effects.
2. Calculating the efficiency attained in the application of ultrasonic waves to membranes.
3. Devising ways to improve the above mentioned efficiency, which probably is low.
4. The use of both much higher frequencies and a broader range of frequencies than those used in this thesis.
5. Application of the fundamentals found to such practical aspects as dyeing, tanning, and impregnating cloth and wood.
INTRODUCTION

Diffusional processes are usually much too slow and cumbersome to deserve serious consideration as an operational method if some other mechanism is available. There are times, though, where the desired product can be achieved only by a diffusion process. These include the tanning of leather, the waterproofing of heavy fabrics, and dyeing. Thermodynamic theory indicates the high economy of diffusion in the separation of solutions. Dialysis is, theoretically, the best method to recover a low concentration solute from a general solution.

The mechanical objection to the above process is their extremely slow rate. Very large equipment is needed to obtain a sufficient output. Dialysis poses the problem of suitable membranes in addition. If it were possible to achieve adequate rates diffusional processes could be adapted to a large number of processes now being carried out by more complicated methods. There is a possibility that sound waves, especially in the high frequency, or ultrasonic range, can be used to increase the rates of capillary and molecular diffusion.

The object of this thesis has been to attempt to improve materially the rate of diffusion in dialysis through the use of ultrasonic vibrations using a frequency range of 12,000 to 30,000 cycles per second. These
vibrations were generated by a magnetostrictive tube
activated by a valve-controlled, oscillating, electrical
circuit.

A more complete outline of diffusion, dialysis,
and the generation and propagation of ultrasonic waves is
included in the Appendix. This section will serve to orient
the reader in a general way as to the scope and purpose of
this thesis.

The diffusivity of a solute through a solvent
and into a mass, as in impregnation, or through a solvent,
across a membrane, and into another solvent, as in dialysis,
depends on many factors. (33) Diffusion through the solvent
depends on the nature of the solvent and solute, their
molecular sizes and weights, on the temperature, the con-
centration, and the presence of other solutes. Diffusion
into a mass depends on the nature of the mass and upon the
size and number of capillaries through it. Diffusion
across a membrane depends on the concentration gradient
across the membrane and also on the physical relations of
the diffusing substance and the membrane. (7), (54)

In all cases, however, rates are too slow to
permit the use of diffusion if an alternate method, such
as distillation or adsorption is feasible. Various ways
are used to speed up diffusion such as rolling and churning
in the case of impregnation, and electrodialysis, or using
an electric field across the membrane, in the case of
dialysis. These methods consume considerable power and
are still unsatisfactory. This thesis has attempted to
achieve greater rates together with lower power demand
by using ultrasonics to promote diffusion. It was be-
lieved that research would lead to a firmer understanding
of the fundamental variables of dialysis and the influence
of ultrasonic waves on dialysis. This understanding could
then be applied to the technical problem of widening the
commercial applications of diffusional processes.

Sound waves appear to be a particularly attractive
means of influencing dialysis since sound waves in a medium
dissipate nearly all of their energy at an interface. This
has been shown by numerous experiments. (11), (34), (38),
(45), (90). As applied to dialysis across a membrane, the
sound energy would be immediately available to promote dif-
fusion and might be expected to result in a rapid pumping
action which would tend to force solute molecules through
the membrane. Other effects of ultrasonics at interfaces
have been widely studied. For example, ultrasonics will
emulsify a two phase water-mercury or water-benzene system,
forming a stable colloidal solution. (34), (68), (82).
The mechanism is probably the tearing of droplets from one
phase and throwing them into the other. Ultrasonic waves
also disrupt small organic bodies such as one cell organisms,
blood corpuscles, and the like. (11), (38), (82). This is most likely due to the inability of the cell walls to withstand the rapidly alternating high and low pressures to which they are subjected.

The propagation of these waves through the liquid follows the laws of wave propagation. The sound energy is absorbed by the liquid it is passing through, this absorption increasing very greatly with frequency (11), (92) but depending also on the medium through which the sound waves travel. (15), (39), (12), (29), (40). In such uses as underwater signaling, detecting and range finding, absorption becomes a serious problem and very high frequencies cannot be used. For experimental and batch work, however, at not too high a frequency, absorption can be ignored in a homogeneous, sound-conducting medium such as water. (61), (72), (84).

Ultrasonic vibrations can be generated through any of several well recognized methods. (32), (34), (47), (55). The design, construction and operation of a suitable apparatus are fully covered in the Appendix. If an oscillating electric circuit has a frequency which is the same as the reasonant frequency of a magnetic rod or tube, the circuit and rod can be inductively coupled to produce large amplitude longitudinal vibrations in the rod. For work in liquids one end of the bar is merely introduced into the
liquid. The vibrations leaving the bar are then transmitted through the liquid. (11), (44), (47), (51), (64), (81)

The data obtained were secured through the operation of equipment of the type described above. Ultrasonic waves were introduced into a sodium hydroxide solution and allowed to impinge on a Cellophane membrane. This membrane separated the caustic from pure water. The effects of ultrasonics were determined by varying both frequency and intensity of sound input and then measuring the effects of these variations upon the rate of diffusion of the sodium hydroxide across the membrane.

No record could be found in the literature that any previous work of this type had been carried out. Therefore, this thesis has been somewhat of an exploratory nature. It is hoped that it will serve to outline the problem so that future efforts can be more easily directed and effectively carried out.
PROCEDURE

Detailed explanations of the construction and operation of the apparatus, the taking of data, and the analysis of the data are included in the Appendix. Therefore, the outline here will cover only the essentials needed to understand the operation.

Drawing on the wealth of information in the literature a magnetostriction ultrasonic vibrator was built with the vibrating tube so arranged so that the ultrasonic waves would impinge directly on a Cellophane membrane. This membrane separated a sodium hydroxide solution from a body of water. Both liquids were kept well stirred at all times in order to eliminate concentration gradients in the bulk of the liquid. Dialysis rates were measured by periodic determinations of the concentration of the sodium hydroxide solution and calculating the rate of mass transfer across the membrane. Several runs without sound waves were made to establish a base rate. After that, a series of runs were made at various sound intensities and frequencies in order to establish the effects of both these fundamental sound variables. A simplified drawing of the dialysis cell itself is included on the next page for clarity. The magnetostrictive nickel tube, N₁, is placed in the liquid in the inner container, L₁.
Simplified Drawing of Dialysis Cell

The ultrasonic vibrations from the nickel, magnetostriiction tube, Ni, travel through the sodium hydroxide solution, \( L_1 \), and impinge on the Cellophane membrane. The effects of the ultrasonic waves are measured by determining the dialysis rate of the sodium hydroxide from \( L_1 \) to the body of water, \( L_2 \), at various frequencies and intensities.
This liquid, the solution of sodium hydroxide, is separated from the liquid in the outer container, \( L_2 \), by a Cellophane membrane stretched across the end of the inner container. The electrical system connected to the magnetocstriction tube is not shown but is so designed that vibrations of varying frequency and intensity can be directed at the membrane.

The data secured in each run were analyzed to determine if they followed the normal dialysis equation:

\[
\frac{dN}{d\theta} = KA\Delta X \tag{1}
\]

\( \frac{dN}{d\theta} \) = transfer rate GM/Min.

\( K \) = membrane constant CM/Min.

\( A \) = membrane area CM\(^2\)

\( \Delta X \) = concentration gradient driving force across the membrane GM/CM\(^3\).

Rapid stirring of both liquids justifies the assumption of complete mixing. Therefore, the concentration gradient may be expressed in terms of total weight of solute and total volume of liquid in each container.

\[
\frac{dN}{d\theta} = KA \left( \frac{N}{L_1} - \frac{N'}{L_2} \right) \tag{2}
\]

\( L_1 \) = liquid in inner container CM\(^3\)

\( L_2 \) = liquid in outer container CM\(^3\)

\( N \) = solute in \( L_1 \) GM

\( N' \) = solute in \( L_2 \) GM.
The total solute in both $L_1$ and $L_2$ must equal the amount in the initial charge to the inner container.

$$N + N' = N_0$$  \hspace{1cm} (3)$$

$N_0$ = total solute introduced in original charge GM

Therefore,

$$\frac{dN}{d\theta} = KA \left( \frac{N}{L_1} - \frac{N_0 - N}{L_2} \right)$$  \hspace{1cm} (4)$$

This is rearranged:

$$\int_{N_1}^{N_2} \frac{dN}{(L_1 + L_2) \frac{N - L_1 N_0}{L_1 L_2}} = \frac{KA}{L_1 L_2} \int_{\theta_1}^{\theta_2} d\theta$$  \hspace{1cm} (5)$$

and integrated:

$$\ln \left( \frac{(L_1 + L_2) N_1 - L_1 N_0}{(L_1 + L_2) N_2 - L_1 N_0} \right) = \frac{KA (L_1 + L_2)}{L_1 L_2} \Delta \theta$$  \hspace{1cm} (6)$$

$N_1$ = solute in $L_1$ at time $\theta_1$ GM  
$N_2$ = solute in $L_1$ at time $\theta_2$ GM

The effects of ultrasonics are determined by noting the changes in the membrane constant, $K$, with changing sonic conditions. Equation (6) is rearranged to solve for $K$ as follows:

$$K = \frac{L_1 L_2}{A (L_1 + L_2) \Delta \theta} \ln \frac{(L_1 + L_2) N_1 - L_1 N_0}{(L_1 + L_2) N_2 - L_1 N_0}$$  \hspace{1cm} (7)$$
RESULTS

The measurements obtained show that, over the range of frequency, intensity, and solution concentration employed, the general dialysis equation is valid. The equation, as noted in the Summary, is:

$$\frac{dN}{d\theta} = KA \Delta X$$

The above equation may be integrated over the time interval used and the calculated transfer rate plotted along with the measured transfer rate. This plot shows excellent agreement between the calculated and experimental values, especially at the longer run lengths which tend to minimize errors in sampling, measuring, and titration. The experimental and calculated transfer rates for all runs are presented in the data sheets in the Appendix together with plots of these values for several of the runs.

The results pertinent to the main object of this thesis, i.e., to determine the magnitude of the effect of ultrasonics on dialysis rates, can best be shown by a table showing the increase in the membrane dialysis constant, K, with both increasing power input to the oscillator and increasing frequency. Table II, on page 16, presents this data. A graph of the same data is given in Figure 1 following Table II. The percent increase in the dialysis coefficient, K, over the base case with no sound is plotted against power input, here used as a measure of sound intensity.
Each line represents operations with a separate magnetostriction tube. The resonant frequency of each tube is given in Table I below.

<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Tube Length Inches</th>
<th>Tube Length Cm</th>
<th>Resonant Frequency Cycles/Sec.</th>
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<tr>
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<td>22.86</td>
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<tr>
<td>3</td>
<td>7</td>
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<tr>
<td>4</td>
<td>5</td>
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<tr>
<td>5</td>
<td>4</td>
<td>10.16</td>
<td>24,500</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>7.62</td>
<td>32,700</td>
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### TABLE II

**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>
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<td>0</td>
<td>0.0280</td>
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<td>3</td>
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<td>0.0332</td>
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<td>32,700</td>
<td>70</td>
<td>0.0380</td>
<td>35.5</td>
</tr>
</tbody>
</table>
FIGURE 1

VARIATION OF DIALYSIS COEFFICIENT WITH POWER INPUT AT VARIOUS FREQUENCIES
DISCUSSION OF RESULTS

The verification of the applicability of the general diffusion equation to dialysis deserves no particular comment as the equation already has ample data to support its general acceptance (33), (37), (46), (54), (67), (77).

The beginning of an apparent plateau in the increase of dialysis constant with increasing power input to the oscillator at constant frequency could be due to either one of, or a combination of, two causes.

1. The efficiency of conversion of electrical power input to sound power output may fall off rapidly at high power input resulting in little added sound power being applied to the membrane after a certain level is reached. There are numerous indications that this may be so in the literature (11), (20). The nickel tube cannot indefinitely increase its amplitude without rupture. While it is not believed that the tube was strained close to this point, the vibrations were powerful enough to etch the face of the magnetostriction tube with the wave pattern typical of cavitation.

2. The efficiency of the utilization at the membrane of the sound power available to promote increased dialysis could also drop at the level where the plateau was observed.

The relative magnitude of each of the above possibilities cannot be evaluated due to lack of pertinent data.
The most straightforward way to determine this would be to construct a set capable of higher electrical power input together with fitting the vibrating tube with a disc or piston of greater diameter than the tube itself. This would greatly increase the sound intensity (47). Declining efficiency in the conversion of electrical to sound power would be indicated if increased power input failed to raise the dialysis rate. Declining utilization at the membrane of available sound power would be indicated if a piston-fitted tube did not increase dialysis rate at a constant high power input.

The beneficial effect on dialysis rate of increasing frequency at constant power input can perhaps be explained by assuming that it is the sound pulse itself and not the power of the pulse which has the greater accelerating influence. This increased effect at the higher frequencies is not unexpected, however, as it has been observed that high frequency sound waves not only have all the properties of low frequency waves, but also usually heighten the effect besides introducing entirely new effects (11), (20), (81), (82). The heightened effect is readily noted here. This leads to the conclusion that perhaps really high dialysis rates could be obtained using ultrasonic frequencies considerably higher than those used in this thesis. Frequencies of the order of 100,000 to 500,000 cycles per second might profitably be investigated.
The data the results discussed above are based on are believed to be accurate. The reproducibility of the various runs was excellent and is discussed fully in the Appendix together with the possible sources of error. The precision with which runs were duplicated can also be seen by examination of Table II in the previous section on Results. Runs 2, 3, 4, 6, 7, 12, and 15 were base runs without sound. All gave dialysis coefficients that are practically identical. Runs 9 and 11 were both run with 10,900 cycles/sec. and 25 watts power input. The coefficients obtained check closely. Runs 28 and 29 were run at 14,000 cycles/sec. and 50 watts. The dialysis constants obtained there check only slightly less closely.

The reproducibility cited above indicates that the several possible sources of error were adequately compensated for. These possible sources include incomplete mixing in the bulk of each liquid, inaccurate sampling, faulty titration of both standard solutions and samples, and inaccuracies introduced in deriving and integrating the mathematical equations used. As mentioned, all these are discussed in the Appendix, together with the methods used to eliminate their effects.

There is not enough data at present to formulate anything more than theories as to why ultrasonic waves do increase dialysis. In order for a solute ion to migrate from one liquid body to the other it must pass three resistances in series, the first being the liquid film on the
solution side of the membrane, the second the membrane it-
self, and the third the liquid film on the water side. If
the ultrasonic vibrations effect a reduction in any one or
more of these resistances, such reduction would mean a higher
dialysis rate. Presumably the two liquid films, having much
the same properties, will react to the sound waves in the
same way despite the fact that one is directly exposed to
the vibrations while the other film is shielded by the mem-
brane. This would probably give no lesser effect to the
protected film as the vibrations easily passed through the
membrane into the lower liquid.

As ultrasonic waves pass through a medium they
create a pattern of alternate high and low pressure bands
moving through the medium. This means that any given point
will be subjected to rapidly alternating compression and ten-
sion. As the vibrations pass through the liquid films it is
conceivable that the alternate compression and tension would
tend to stir up the film and thereby cause it to lose its
static form and become part of the turbulent bulk liquid.
As the ultrasonic intensity is increased the film will become
less and less static and finally practically disappear as an
effective resistance to diffusion.

This theory can explain the observed plateau at a
power input of 1.41 watts per square centimeter of membrane
area where increasing power input, or sound intensity, did
not further increase the dialysis rate. It is possible that
up to that power input increasing ultrasonic intensity resulted in greater disruption of the liquid films and the lower resistance gave higher dialysis rates. At the top power input, however, the liquid films, being practically destroyed, offered little or no resistance to dialysis. Since liquid film resistance is then negligible, greater intensity vibrations cannot serve any useful purpose and the dialysis rate stays constant.

The hypothesis that increasing sound intensity decreases liquid film resistance does not explain why increasing frequency will also increase dialysis rates. Especially at high intensities, where, theoretically, the liquid film is practically destroyed, increasing sound frequency should have no effect. The apparent effect of frequency may be explained, however, by the hypothesis that frequency is chiefly effective in lowering the resistance to diffusion of the membrane itself. The increase in dialysis rate through the membrane could well be caused by a sound induced flexing of the membrane. This flexing may promote a pumping action which in turn would tend to substitute convection currents for true diffusion. Due to molecular bonds and intermolecular forces, this flexing would have a definite maximum amplitude short of rupture. A low sound intensity, or power input, should be sufficient to achieve this maximum degree of flexing. Therefore, increasing sound power would have no effect on the membrane resistance. However, increasing sound frequency would increase the
number of flexes per unit time, increase the pumping action, and consequently increase dialysis rate through the membrane itself.

To recapitulate, the theory has been advanced that sound intensity is the predominant variable in reducing liquid film resistance while sound frequency is basically effective in determining membrane resistance. It is realized that conclusive data do not exist at present which will either prove or disprove the theory. However, a series of experiments, devised in the light of experience gained in this thesis and designed to supply the needed data are outlined in the section on Conclusions and Recommendations that follows.
CONCLUSIONS AND RECOMMENDATIONS

This thesis has served to open up the field of the use of ultrasonics to promote diffusion and dialysis. While the results reached are of only negative value insofar as commercial applications are concerned, it is believed that the investigation is of theoretical interest. Regarding the work done here as of an exploratory nature, the way is now clear for clearly planned experiments which can determine and measure the effects of the fundamental variables involved.

The logical assumption is that frequency and intensity are the important variables that determine the effects of sound waves in any given situation. An experimental program could be set up to ascertain the effect of each of these. Frequency is very easy to attain and control. Any desired frequency is reached by using the proper length magnetostriction tube and by tuning the oscillating, electric circuit to resonance. Sound intensity, however, would be more difficult to measure. In this thesis electrical power input was used as an indication of sound intensity. The intensity most useful for experimental work would be the actual intensity of the sound waves as they travel through the solution and strike the membrane. This sound power is related to the electrical power input through the efficiency of changing electrical energy in the mechanical energy of the vibrating rod and also the efficiency of changing that mechanical energy into sound energy. As can be seen from Figure 1 in Results,
increasing power input at constant frequency always increased dialysis rate. It seems evident, therefore, that sound power does increase with electric power provided the frequency remains constant. The equipment used in this thesis could not be used to measure if, at different frequencies, the same electric power input would give the same sound power output. Indeed it would appear that it would not in view of the findings of other investigators that power output falls off sharply with increasing frequency \((13), (20), (58), (62)\). This would indicate that higher frequencies are even more effective in increasing dialysis rates than is suggested in Figure 1. Therefore, any further work should start with a series of runs, using the generator to be used throughout all runs, to determine the actual sound power output at a variety of frequencies and input power levels. This could be accomplished by measuring the radiation pressure of the signal. Perhaps a better way would be to send a sound signal through a medium and then receive and measure the loudness of the signal a known distance from the sending instrument. The sound absorption of the transmitting medium would have to be compensated for. Such measurements have been made on numerous occasions and the absorption coefficients for many compounds are reported in the literature \((8), (16), (17), (41)\).

Knowing the frequency and intensity of the sound waves given off by the set permits rapid determination of the effects of these variables. A series of experiments
such as those carried out in this thesis would be sufficient. A basic difference would be to run experiments at constant frequency at known sound power output instead of known electric power input. Similarly, experiments varying frequency would be run at constant sound, instead of electrical, power.

Unfortunately, knowing the effects of frequency and intensity in one dialysis cell does not permit understanding of the causes of these effects. Ultrasonics must increase the dialysis rate by reducing one or more of the three diffusion barriers. These are the membrane itself and the liquid film on either surface. However, no intelligent extension of ultrasonics to a different type of dialysis cell can be made without knowledge of the manner in which these barriers are broken down. Further experiments are needed to supply this knowledge. A program designed to test the theory outlined in Discussion of Results is outlined below. This theory presupposes that sound intensity is largely responsible for reducing liquid film resistance while sound frequency influences membrane resistance. Increasing either variable decreases the corresponding resistance.

The most straightforward way to test the above theory is to run ultrasonic-influenced dialysis experiments in two carefully chosen dialysis cells. In one of these cells a low resistance (high dialysis constant) membrane would separate two viscous liquids. Since diffusion through a liquid film is slowed by increasing liquid viscosity, (33),
(48), (53), (67), this will throw a larger than usual share of the total resistance into the liquid films. If sound frequency has little or no effect on the liquid films, increasing frequency would not increase dialysis rate to the same extent as in the Cellophane-water cell. If increasing sound intensity does lower liquid film resistance, then a heightened effect of intensity will be noticed in such a cell.

The second cell would be at the other extreme with two fluid liquids separated by a membrane with a lower dialysis constant. In this case the theory would indicate that sound frequency would be the controlling factor with sound intensity of secondary importance.

Even if the proposed theory proved incorrect, the data secured by carrying out the program outlined above would most probably be sufficient to segregate the two effects and to determine the causes of their effects.

A short outline of the program is presented below:

1. Determine the relationship between sound power output and electric power input for the ultrasonic generating set to be used and over the proposed frequency range.

2. Measure dialysis rates both without sound and with various frequencies and intensities in a dialysis cell in which the liquid films are a
known major part of the total diffusion resistance.

3. Repeat the experiments made above but in a dialysis cell in which the membrane is a known major part of the total diffusion resistance.

The outlined program should enable the researcher to determine the effects and the causes of the effects of both sound frequency and intensity over the ranges of frequency and intensity used. From a research point of view, the ranges selected are not important. However, if industrial applications are a consideration, it is recommended that much higher frequencies be used than were employed in this thesis. All indications were that high frequencies were much more efficient than low in increasing dialysis rate. It might be that ultrasonics of the order of 100,000 or more cycles/second would give attractive dialysis rates. Since magnetostriction tubes become very short and hard to handle at 30,000 to 40,000 cycles/second, the magnetostriction generator would have to be abandoned and a piezoelectric crystal generator employed. Generation of ultrasonic waves with a piezoelectric quartz crystal is discussed in the Appendix. An added advantage is that the piezoelectric generator is much more efficient than the magnetostriction tube at high frequencies (20).
It would be best to outline the theories covering diffusion before considering how ultrasonic vibrations can be applied. Diffusion is generally believed to be due to the random thermal motion of individual molecules \((48), (53), (54), (67), (77)\). Molecules in a body such as water are comparatively free to move about and, unless outside influences interfere, will tend, in time, to form a homogeneous mixture. Diffusion in a gas or liquid is considered by idealizing a plane through the fluid. If more of one type of molecule are on one surface of this plane than the other, random thermal motion will tend to send more molecules across the plane from the high concentration side than will come the other way from the low concentration side. This will tend to equalize the concentrations and therefore net diffusion in a homogeneous medium is said to depend on a concentration gradient in the medium. It should be emphasized that diffusion is constantly taking place even with no gradient. However, the rates are equal in all directions and no net diffusion or transfer of material takes place.

To be rigorous, activity gradient should be used instead of concentration gradient as the so-called driving force behind diffusion. This is shown by a system in which two immiscible liquids each contain the same solute. This system can be at equilibrium with no net diffusion of solute across the liquid interface despite a very sharp concentration
gradient across the same interface. The activities are equal though, and therefore no activity gradient exists under these conditions. In fact the addition of further solute to the low concentration liquid will set up an activity gradient opposed to the concentration gradient and a net transfer will take place from low to high concentration. However, activity must be considered only in a few cases. In the great majority of practical situations, net diffusion takes place from high to low concentration and the concentration gradient is an adequate measure of its rate. Therefore, diffusional processes are usually thought to follow equation (8) below. Consistent units must be used.

\[
\frac{dN}{d\theta} = D A \frac{dC}{dx} \tag{8}
\]

\[
\frac{dN}{d\theta} = \text{rate of net mass transfer, gm./min.}
\]

\[
D = \text{diffusivity, cm.}^2/\text{min.}
\]

\[
A = \text{total cross section at right angles to direction of mass transfer, cm.}^2
\]

\[
\frac{dC}{dx} = \text{concentration gradient across A, gm./cm.}^3/\text{cm.}
\]

Several theories have been advanced to explain the actual mechanism of diffusion. One of these, (60), is a molecular model which regards viscosity and diffusion as fundamentally the same process. It is assumed that the model for diffusion is precisely the same as that for viscous flow—a single molecule jumping from one lattice position to another through the liquid. The migrating molecules make use of
available holes in the liquid. In most liquids flow rate is determined by available holes in the liquid, not energy of activation needed to surmount barriers to get to the hole. Necessary hole size would be one-sixth the molecular volume for ordinary liquids, and one-twentieth the molecular volume for liquid metals. If expansion of substances on melting is considered to be hole formation, one-sixth and one-twentieth is generally found to be the normal expansion of volume. In long molecules it is probable that flow takes place by segments rather than by the molecule as a whole. Definite evidence for this is that observed heats of activation are independent of chain length for homologous polymers.

Another theory, (33), goes further and attempts to analyze diffusion of gases and liquids into solids and semi-solids immersed in the fluid. This is a very complicated field. The tanning of leather is an example. Here diffusion can take place through either capillary action or strict diffusion in the space between the fibers and by diffusion through the fibers themselves. The complex mechanism has discouraged any appreciable study of this type of diffusion and the tanning of leather remains largely empirical. Most solid diffusion studies have been on gases through metals or, in some cases, gases through membranes. Even in diffusion through crystalline solids complicating factors are introduced due to the existence in the solids of rifts due to mechanical defects and of interfacial surfaces. This
gives rise to at least two methods of diffusion with, probably, very different rates. One is homogeneous diffusion through the crystal lattice. The other is diffusion along grain boundaries and crystal interfaces. The mechanism of such diffusion is not positively known. It could be the diffusion of individual molecules into empty lattice positions or the rotation past each other of a pair of atoms. This last would necessitate additional volume formation which could come from compression of neighboring atoms. The fact that diffusion through metals is dependent on the purity of the metal indicates that there is lattice diffusion. A pure metal would set up a tighter lattice with less empty positions than an alloy. Therefore, lattice diffusion through an alloy would be expected to be more rapid and the data substantiate this.

The work on the diffusion of gases through membranes such as rubber, resins, and plastics, mentioned in the above cited reference, (33), was of particular interest to this thesis. The data indicate that perhaps the molecules change from the normal to an activated state. The relatively high activating energies noted, together with the deterioration with time of the membrane material, imply that diffusion through membranes of the plastic polymers is accompanied by the breaking of polymer bonds. This possibility was not investigated by this thesis. In order to forestall possible membrane deterioration, the Cellophane membranes were replaced
after four or five runs with the last run on each membrane being a check run with no sound to determine if the base dialysis content was still valid. None of the check runs indicated that the membranes had changed.
DIALYSIS

Dialysis is that field of diffusion in which a substance in solution diffuses through a membrane. According to thermodynamic theory, dialysis is the ideal method for the separation of solutions as energy requirements are practically zero. If suitable selective membranes could be found, all distillation and extraction processes could be very efficiently carried out by dialysis (7). An ideal use for dialysis would be the separation of the two solutes in a solution by the diffusion of one through a membrane which would not pass the other. Dialysis as a process was inspired by osmosis and is of course indispensable in animal and plant life. However, the lack of membranes that will perform satisfactorily and the extremely slow rate of those available has strictly limited the application of dialysis to industry.

The beet sugar and the paper and rayon industries are perhaps the greatest users of dialysis. In order to extract the sugar from the beet cells the beets are sliced very thin and then placed into hot water. The cell walls act as a membrane which will pass the sugar and retain the remaining cell material. In paper and rayon manufacture cellulose and alkali are reacted to give alkali cellulose. It is desirable to recover the valuable excess alkali which is contaminated with soluble hemi-cellulose and other extracted material. Dialysis is used to extract it as the
alkali ions will pass through a membrane which will retain the large organic molecules.

Dialysis is also used in the purification of clays which are to be activated (54).

Several methods have been tried to achieve higher dialysis rates. Electrodialysis is ordinary dialysis with an electric field set up across the membrane to speed reaction. This method, however, is much more expensive due to the electrical power consumed and also introduces the complications of electrolysis. Baral(7) tried to save this expense and trouble by setting up an electric field across the membrane with the terminals entirely outside the solution. In this way higher rates are obtained with electric current considerably reduced. Nevertheless, dialysis rates still are not adequate.

This thesis has made another attempt to improve dialysis rates through the use of ultrasonic vibrations with results that are discussed in the main body of this report. In view of the other, unsuccessful attempts to achieve high dialysis rate, further effort might seem unjustified. However, ultrasonics represented a fresh approach and it would be a great technical advance if dialysis rates could be substantially increased. The power supply of an ultrasonic generator is less than that used in the rolling and splashing employed in tanning leather and is greatly less than the
heat requirements of a distillation column. This leads to a survey of the generation and propagation of ultrasonic waves.
The theory of sound is well covered in many excellent books such as the "Textbook of Sound", by A. B. Wood (81). For completeness, however, a discussion of vibrators will be included here.

Consider first the vibrating characteristics of an elastic mass. This mass will vibrate ordinarily a definite natural frequency but with constantly decreasing amplitude. This natural, or free, frequency is determined by such factors as the dimensions, material, and temperature of the mass, and is called the resonant frequency. The constantly decreasing amplitude is caused by damping which results from energy losses to the surroundings and from mechanical losses within the vibrator. A rough sketch of amplitude against time for damped, free vibration is shown below.
The logarithmic decrement of damping is the common measure of damping. It is the log of the ratio of successive maximum amplitudes, these being on opposite sides of zero displacement. In equation form it is:

\[ M = 0.217 \frac{k\chi}{N} \]

\[ M = \log \text{decrement} \]
\[ k = \text{damping constant} \]
\[ N = \text{natural frequency} \]

Since damping eventually eliminates free vibration, a mass can be maintained in vibration only by application of a periodic force. This force may or may not have the same period as the free vibrator. The mass will ultimately vibrate with the frequency of the impelling force and not with its own free frequency, if these frequencies are different. Such vibrations are called forced vibrations. The effects of free and forced frequencies and of damping can be illustrated by an example. Consider a rod vibrating longitudinally at its free frequency with no damping. At zero damping there is no energy loss. Therefore, the amplitude remains constant. Now if a forced vibration of the same frequency is impressed on the rod, it will be seen that the amplitude will steadily increase and finally become infinite. This, of course, can never happen in practice for the damping is never zero.
For small values of damping, the amplitude is greatest when the forced frequency coincides with that of the free vibration. This condition is known as resonance. As resonance is approached the effect of damping becomes noticeable and the phase change through resonance becomes more abrupt with decreased damping. In fact the abruptness of this phase change can be used to measure the sharpness of resonance and the degree of damping in a vibrating mass. The more abrupt the change the smaller the damping and the sharper the resonance. The damping becomes relatively more and more powerful in its influence as resonance is approached. At resonance the amplitude and power dissipation reach their maximum values. The ratio of actual output to maximum output in terms of forced frequency and natural frequency is given by:

$$\frac{W}{W_{\text{max.}}} = \frac{4k^2p^2}{(N^2-p^2)^2 + 4k^2p^2}$$

(10)

$W =$ output
$k =$ damping constant
$N =$ natural frequency
$p =$ forced frequency

The energy dissipation at resonance falls to half value when the forced frequency departs from the natural frequency by the fraction $k/N$. This indicates that the smaller the damping (small $k$) and the greater the natural frequency, the more rapidly will the dissipation fall off on either side of resonance—that is, the sharper will be resonance.
A well balanced tuning-fork is a good example of sharp tuning when it may be excited through the medium of surrounding air by the vibrations of a second fork adjusted to the same frequency. When the two forks are closely in tune there will be a very marked response; otherwise there is relatively little effect. Even sharper tuning is required in the case of quartz resonators and oscillators which have extremely little damping and high natural frequency.

The velocity of wave transmission depends solely on the physical properties of the medium, elasticity and density being the important considerations. Frequency and amplitude should have no effect on velocity. Some investigators (78) seem to have found a slight increase of velocity with increased frequency in carbon dioxide but such results have not yet been substantiated. Large amplitude can change velocity by causing density effects. The sound velocity in the immediate vicinity of an electric arc is much higher than normal velocity at ambient air temperature and pressure (70). As a result of many photographic studies, it is known in a general way that the sound wave from a spark consists of a single pressure pulse which is propagated with a velocity initially greater than normal velocity at the ambient air temperature, but which soon attenuates to near normal velocity within some centimeters from the source. The distance required depends upon the total energy input but to a greater extent to the rate of energy input. The peak pressure in the
sound pulse may be very high, some calculations putting the pressure near the source of an exploding wire at 40 atmospheres.

There is considerable literature on the general field of ultrasonic theory, generation, and application, even though none could be found on the specific problem of using ultrasonics to promote dialysis. The theory of sound has been briefly reviewed above insofar as it concerns this thesis. Ultrasonic waves may be generated by any one of several methods. These include:

1. the Galton whistle
2. the Hartmann acoustic generator
3. a magnetostriction vibrator
4. a piezoelectric vibrator.

The applications of ultrasonic waves are discussed in the section after those on generation.

AIR-JET GENERATORS

The Galton whistle and the Hartmann generator can be used only to give vibrations in gases. As they are seldom, if ever, used in experimental work and are fully described in the literature, they will not be reviewed here (11), (35), (81), (82), (92).

THE MAGNETOSTRICTION EFFECT

The information given in this discussion of the magnetostriction effect and the following discussion of the piezoelectric effect has been obtained through reference to
the literature selections cited in the bibliography of this thesis. However, since the information is part of the common lore of sound generation, literature references have been, for the most part, omitted.

The magnetostriction effect shown by magnetic materials is the basis of all magnetostrictive oscillators. If a rod or tube of ferromagnetic material is brought into a magnetic field parallel to its length, the tube length is changed slightly; this change of length is independent of the sign of the field, and may be either a decrease or increase, depending on the nature of the material, its previous treatment, the degree to which it was previously magnetized, and the temperature. This phenomenon is known as "magnetostriction" or the Joule effect, after its discoverer. The changes of length so produced are comparatively small, the relative change of length being of the order of one part per million per gauss, and can only be determined by the microscope or by an optical lever. The magnetostriction effect decreases with rise in temperature, and disappears at the Curie point, where the material loses its magnetic properties.

The fundamental and harmonics can readily be obtained almost pure; that is any particular harmonic can be excited free from the others and free from any transverse vibration of the bar. The resonance is extremely sharp (indicating extremely small damping forces in the bar) and careful tuning is required. A thin disc of soft iron firmly
cemented to the end of a bar of non-magnetic material (like glass) may similarly be employed to excite resonant vibrations in the non-magnetic material.

Like most physical phenomena, magnetostriction is reversible. If a previously magnetized rod of nickel is stretched, the magnetization of the rod is decreased; if the rod is compressed in the direction of its length, the magnetization is increased. If a coil is put around the rod, an electromotive force is induced in it by an elastic deformation of the rod.

The fundamental frequency of a vibrating rod is:

\[ N = \frac{k}{2} \sqrt{\frac{0.81 \times 10^5 E}{\rho}} \]  

(11)

- \( N \) = fundamental frequency cycles/sec.
- \( k \) = order number of overtone = 1, 2, or 3, etc.
- \( l \) = length of rod, cm
- \( E \) = modulus of elasticity, kg/mm²
- \( \rho \) = density, gm/cm³

Total amplitude is approximately one ten thousandth of the length of the rod. Power output falls off with increasing frequency.

When magnetostriction tubes are used as vibrators the longitudinal vibrations are set up in the magnetic bars by placing them in a magnetic field alternating at the resonant frequency of the bar. The longitudinal vibrations of magnetostriction bars have been employed to produce and
control electrical oscillations over a frequency range from a few hundred to more than three hundred thousand cycles per second. The oscillations are set up by a coil carrying alternating current (from a valve oscillator) that surrounds the bar. The alternation in magnetic field in the coil induces corresponding alternations in the length of the bar. The best effects are obtained when the bar is initially magnetized by means of a second coil carrying direct current. At resonance the oscillations set up may attain a considerable amplitude. If the exciting coil forms the inductance in the tuned plate circuit of the valve, and a galvanometer is inserted in the grid circuit containing a coil coupled to the plate coil, the variations in the deflections of the grid galvanometer give definite indications of resonance in the bar. This method is particularly useful at ultrasonic frequencies, as the increased power output cannot be heard.

The constancy of frequency obtained by such interaction of a magnetostriction bar and the electrical oscillations of a valve circuit compares favorably with the oscillations from piezoelectric crystal generators. (See below.)

MAGNETOSTRICTIVE MATERIALS

The metals used in magnetostrictive oscillators are the common magnetic metals. Nickel is commonly used due to its high motional impedance and low eddy current loss. Metal alloys approximately thirty-six percent nickel and sixty-four percent iron give good results. Nichrome, made of nickel,
chromium, and iron, and Monel metal, composed of sixty-four percent nickel and the rest copper, iron, and manganese, also form powerful oscillators. Duralumin has also been used in a very powerful type of oscillator built by H. W. St. Clair (64). Another possibility among the metals produced in quantity is Invar.

When using magnetostriction rods the following general considerations apply:

1. The rod will vibrate most actively at its natural resonant frequency. This natural period is determined by the composition, physical properties, and dimensions.

2. When the rod is vibrating at its natural fundamental (no overtones) there is a nodal point at the center. It is here that the greatest stretch occurs and the greatest magnetostrictive changes of flux take place. Therefore, the exciting coils should be near center if possible.

3. The rod supports should be at the node so as to give as little interference with the vibrations as possible.

4. Long thin coils with little clearance should be used to excite the bar. The long-thin coil gives more efficient magnetic coupling while the small clearance promotes the fundamental over the harmonic overtones (51).

A rod of nickel when magnetized shortens by about one millionth of its length for a magnetizing field of one gauss. This is the observed fact when the magnetization is
produced by a steady magnetizing force. The change is thus very small for the reason that it must take place against the elastic force of the rod. When the rod is magnetized by a force that increases and decreases in an oscillatory manner at a period resonant with the period of the body, the change in length may be more than one hundred times as great as that obtained with the same amount of direct current applied. The expansion and contraction in this case are not opposing the elastic force of the rod, but only its viscosity.

The frequency of magnetostrictive vibrations is affected by temperature. It would be desirable to achieve a zero temperature coefficient of frequency but this is virtually impossible since it is affected by the temperature change of expansion, the temperature change of sound velocity, and the temperature change of elasticity. The temperature coefficient of frequency of magnetostrictive rods is about one fiftieth of one percent per degree centigrade.

Physically, magnetostrictive rods are very handy to use. It is a simple matter to have a set of rods for variable frequencies and each rod can be easily ground to within a few cycles of the desired frequency. Shortening the rod increases the frequency. The rods are also very constant with such variations as changing circuit constants, battery voltages, and the like.
As do all magnetic materials, magnetostrictive bars exhibit hysteresis and eddy current losses. In a bar these losses result in considerable heating which will change the vibrating frequency and finally cut oscillation off entirely. This tendency is countered by two methods; first, cutting down the power losses and, second, by cooling the metals to maintain constant operating temperature. Using a thin walled tube with a longitudinal slit will reduce power losses considerably but the tube will still heat up and cease oscillating. Using a water jet inside the tube will effectively remove the generated heat and permit operation over extended lengths of time. The thinner the tube wall and the larger the tube diameter, the higher motional impedance will be and the less eddy current loss.

A MAGNETOSTRICTION OSCILLATOR

All oscillators using the magnetostrictive effect are basically nothing more than the interaction of a magnetic bar and an alternating, electrically induced, magnetic field.

On account of the extensive use of electrodynamic or electromagnetic forms of sound generators and receivers, it is a matter of some importance to note their characteristics and efficiencies. In any form of machine which converts electrical energy into motion, the moving mechanism reacts on the electrical circuit. In the case of an ordinary electric motor, for example, a back E M F is developed in the armature when the latter rotates. The electrical efficiency
of the motor is equal to the ratio of this back emf, $E$, to the voltage, $V$, of the supply, since $VI$ is the gross power supplied and $EI$ the power utilized. The current, $I$, through the armature is equal to $V-E/R$ which consequently becomes smaller the greater the efficiency of the motor, i.e. the nearer $E$ approaches $V$. The back emf therefore behaves like an added resistance in the circuit. Denoting this apparent additional resistance due to the rotation of the armature by $R$, we may write the current, $I$, equal to $V/r+R$. Now the power supplied is $I^2(r+R)$ and the power utilized is $I^2R$, whence the efficiency is $R/r+R$. The efficiency is therefore the ratio of the motional resistance $R$ to the total effective resistance $r+R$. The net power utilized by the motor is a maximum when $R=r$ in which case the efficiency is 50%.

In a similar manner, the mechanical vibrating element of an electrical sound generator or receiver reacts on the electrical circuit. The back emf produced by the vibrations manifests itself as a change of impedance in the circuit and the characteristics of such a vibrator can be determined from the analysis of its impedance at different frequencies of excitation. The principle involved is analogous to that of the direct current motor. The only difference is that here impedances and phase angles are dealt with instead of the ordinary D.C. resistances. Thus, in such an electrically maintained vibrating system, if $R'$ and $L'$ are the vibrating values and $R$ and $L$ the stationary values of
resistance and inductance, then \((R' - R)\) is the motional resistance, \((L'p - Ip)\) or \((X' - X)\) the motional reactance, while the motional impedance is the vector sum of \((R' - R)\) and \((X' - X)\). When the impressed frequency differs widely from the resonant frequency of the vibrating system, the amplitude of the vibration will be small for a given input of electrical energy. Under such circumstances, therefore, the motional impedance may be small and the efficiency very low. Near resonance, however, in a well designed sound transmitter, the motional impedance may be large and the corresponding efficiency high. As in the core of the electric motor, the ratio of the maximum motional resistance to the total effective free resistance is a measure of the efficiency at resonance. The free resistance is measured with the vibrator free to move instead of clamped, or heavily damped, in the normal position. If the power of a sound transmitter is sufficiently large, the output and efficiency may be determined with sufficient accuracy by a more direct method. Measuring the electrical power consumed in the circuit by a wattmeter at a series of frequencies near resonance, it will be found that a marked increase occurs at resonance. A typical curve is shown.
The alternating current is easily supplied by a resonating circuit. Such circuits are widely used in all types of radio and electronic work and are usually set up with a fixed inductance and a variable capacitance (44), (71). The thermionic valve gives the best and easiest source of alternating current for sound production. Its simplicity, wide range of power and frequency, steadiness of operation, and flexibility has made the valve standard equipment for such circuits.

A typical resonating circuit is shown in Figure Al on the following page.

An inductance coil $L_g$ connecting the filament $F$ to the grid $G$ is coupled inductively to another coil $L_p$, connecting the plate $P$ to the filament through a high tension battery $B$. Battery $P$ merely serves to heat filament $F$. A variable condenser $C$ is connected in parallel with the plate
FIGURE A1

TYPICAL RESONANT ELECTRIC CIRCUIT
coil $L_p$. In alternative arrangements this condenser may be connected across the grid coil, or condensers may be used with both grid and plate coils. A third coil $L_e$, coupled to the coils $L_p$ and $L_g$, provides the AC for the external circuit. This coupling is not clearly shown in the drawing. Briefly the system functions as follows. A small oscillation set up in the tuned circuit $L_p-C$ either by switching on the filament current or the high tension battery, induces a corresponding change in the grid coil which consequently causes the potential of the grid relative to the filament to fluctuate in the same manner. In turn this varies the plate current, giving an amplified voltage fluctuation in the plate $L_p-C$ circuit, thereby increasing its oscillations. The grid is again affected, and the cycle continues to repeat itself until a steady state of oscillation is maintained. Regarded in this very elementary manner the frequency of the oscillation is dependent solely on the values of $L_p$ and $C$ in the plate circuit giving a frequency equal to $1/2\pi \sqrt{L_pC}$, provided the resistance $R$ of the plate coil is not too great. A more complete view of the matter includes the effect of mutual inductance $M$ between the plate and grid coils, as well as the amplification factor $\alpha$ and "plate" resistance $\rho$ of the valve itself. The valve adds to the resistance $R$ in the oscillatory circuit a term of the form $(L_p+\rho M)/\rho C$ the equation of oscillation being:
\[ L_p \frac{d^2i}{dt^2} + (R + \frac{L+iM}{\rho C}) \frac{di}{dt} + \frac{i}{C}(1+\rho) = 0 \] (12)

where \( i \) is the current flowing in the plate inductance coil \( L_p \). The damping constant is:

\[ k = \frac{1}{2L} (R + \frac{L+iM}{\rho C}) \quad (13) \]

and the frequency of oscillation, when damping is small:

\[ N = \frac{1}{2\pi\sqrt{L_pC}} = \frac{n}{2\pi} \]

where \( R \) is small compared with \( \rho \) as is usually the case in practice. The condition for oscillation requires that \( n^2 \) should be always greater than \( k^2 \).

If it is required that an oscillator should give a maximum power output at a particular frequency, it is an advantage to divide the inductance \( L_p \) in the tuned circuit into two parts, \( L_p \) and \( L' \), one of which, \( L' \), is introduced in series with the capacity as shown. This amounts to connecting the plate to a suitable tapping point on the inductance \( L_p \) in the tuned circuit.

The frequency of an oscillator is conveniently adjusted by means of a set of condensers, from a variable air condenser 0.001 microfarad to large capacities of the order of 10 microfarads in mica or paraffin paper condenser. It is convenient also to have a series of pairs of inductances suitable for different ranges of frequency as 1 henry for
frequencies from 200 to 1000 or 2000, 10 millihenries for the order of 10,000 and so on. A set of coils made for radio-telephony will cover the higher frequency ranges. There are numerous commercial forms of valves which are suitable for oscillators having power outputs from a few watts to many kilowatts. Loudspeaker type valves are useful where moderate output, around 10 or 20 watts, is desired.

In the circuit described above the magnetostrictive rod could be placed inside the coil $L_e$. One of the earliest magnetostriction generators was designed by G. W. Pierce (55), (56), (58). It contains a reaction circuit together with a valve and is shown in Figure A2 on the following page.

The rod $S$ is damped in the middle between two knife edges, and around it on the right hand side is the coil $L_1$ forming with the condenser $C$ an oscillating circuit connected to the anode of the valve $R$. On the left hand of the rod we have the coil $L_2$ connected to the grid and filament of the valve.

The internal diameter of both coils is great enough to allow the rod to move lengthways freely. This circuit gives self-excitation of oscillation by the reciprocal effects of magnetostriction, for as the elastic deformation of the rod produces a change in its magnetization, an EMF is induced in the coil $L_2$, which regulates by means of the grid the anode current of the valve. Oscillation is indicated by a rise in
FIGURE A2

DESIGN OF A MAGNETOSTRICTION OSCILLATOR BY G. W. PIERCE
the anode current on the milliammeter A. In this apparatus the premagnetization of the rod is produced by the steady anode current or by a permanent magnet placed near the rod.

Perhaps the best vibrator yet designed for high frequency vibrations in gases is the apparatus of H. W. St. Clair of the U.S. Bureau of Mines. He used his apparatus to clear soot and smoke from flue gases (64). It was designed on the loudspeaker principle and used a large Duralumin cylinder as the vibrating element.

No difficulty is experienced in introducing the vibrations into the medium where they are to be used. As in the case of the oscillator just described the vibrating element need only be introduced directly into the medium and the vibrational energy of the metal is transformed directly into the surroundings as sound energy.

THE PIEZOELECTRIC EFFECT

In 1880 the Curie brothers first demonstrated the phenomena that is the basis of all piezo-crystal oscillators. This type oscillator has been more widely employed than any other up to the present time and has only recently started to be supplanted by the more universal magnetostriction oscillator. Fundamentally the piezoelectric effect is the development of electric charges on definite crystal surfaces of many crystals when these crystals are subjected to pressure or tension. The effect appears in crystals of the most various systems. Among others it has been observed in
tourmaline, quartz, zinc blends, sodium chlorate, tartaric acid, cane sugar, and Rochelle salt. The electrical charges set free and appearing on the surfaces are proportional to the mechanical pressure or tension and the sign of the charge changes when a pressure is changed into a tension.

The effect is perfectly reversible and gives rise to the reciprocal piezoelectric effect whereby a piezoelectric crystal, placed in an electric field of force in such a way that the direction of the field is the same as the direction of the piezo axis, will expand or contract in certain directions.

Of all the available crystals, quartz is used almost exclusively as it best combines sufficient piezoelectric action with adequate mechanical strength. Tourmaline plates are sometimes used. Rochelle salts have a piezoelectric effect about 1000 times greater than quartz but are not used in sound generation due to poor stability under high voltages and continual operation (34). All discussion following will assume a quartz plate as the vibrator. Most crystals are circular, the diameter being roughly proportional to the desired electrical input. A rough approximation gives one inch of diameter per kilowatt input.

If a properly cut quartz crystal is placed between the plates of a condenser connected to a source of alternating current, the quartz will be compressed in one half of the cycle of the field and expanded the same amount in the
other half (11). There will be no change of crystal volume during the oscillation as a change of one dimension is compensated for in another. The alternating charges on the condenser plates will set the quartz into elastic oscillations of the same frequency as the field. When the electric frequency and the natural mechanical frequency of the plate are in resonance the amplitude and power output will be a maximum.

In the case of thickness vibrations, the natural elastic frequency of the fundamental may be easily calculated if the influence of transverse vibrations are ignored; that is taking the plate as infinitely large.

\[ N_o = \frac{\sqrt{c}}{2d} \sqrt{\frac{c}{\rho}} \]  \hspace{1cm} (15)

- \( N_o \) = frequency
- \( d \) = thickness (cm.)
- \( \rho \) = density g/cm.\(^3\) = 2.65
- \( c \) = characteristic modulus of elasticity
  \[ = 85.46 \times 10^{10} \text{ dyne/cm.}^2 \]

\[ N_o = \frac{285.500}{d} \text{ cycles/sec.} \]  \hspace{1cm} (16)

In plates of limited size the resonant thickness frequency is changed somewhat by coupling with longitudinal vibrations. Investigations by Hund give the resonant frequency to be

\[ N_o = \frac{287 \pm 5}{d} \text{ kc/sec.} \]  \hspace{1cm} (17)
The sharpness of resonance of quartz vibrating in air is extremely great. The logarithmic damping is of the order of $10^{-4}$. Damping increases in general with decrease in the velocity of sound, and is greatly dependent on the condition of the surface of the crystal. On account of the low value of the damping, very exact tuning between the exciting alternating voltage and the natural frequency of the quartz is necessary. On account of this sharpness of tuning, quartz plates vibrating at resonance frequencies are used in high frequency work as standards of frequency, for controlling transmitters, and as stabilizers for oscillating circuits.

The upper limit of frequencies attainable by means of piezo quartz vibrators lies at about 50,000 kc/sec. The plate cut at right angles to the piezo axis is in this case only 0.059 mm. thick and hence very fragile. Also the plate may be broken down electrically by a too powerful field and so destroyed. In order to attain still higher ultrasonic frequencies with piezo-electric crystal plates, no other course remains but that of producing overtones in plates of a lower natural frequency. The energy output of the plates then becomes less, but on the other hand they may then be excited with considerably greater electric energy without risk of destruction. A further advantage is that a number of different frequencies may be produced by a single plate.
PIEZOELECTRIC GENERATORS

There are many practical designs of piezo-quartz oscillators in the literature. The same undamped electric oscillations are used as in the magnetostriction oscillators.

The connection between the quartz and the electric generator may be made in a variety of ways. The simplest way is to use a Hartley type oscillator with the quartz in parallel with the capacity of the oscillating circuit. The circuit is tuned into resonance with the quartz by means of the variable condenser. This type of connection for the quartz particularly useful when powerful vibrations, especially in liquids or solids, are to be generated, and is shown in Figure A3.

A typical piezoelectric crystal generator is shown in Figure A4. It will be noted that the electrical connections are practically identical with those shown for the magnetostriction oscillator in Figure A1. For clarity the same nomenclature has been used. Since the reciprocal piezoelectric effect, and hence the amplitude of vibration of the quartz, is proportional to the voltage applied, it is useful to transform up the alternating voltage produced by the electric oscillator. As is shown in the drawing, coil \( L_e \) not only couples the quartz crystal \( Q \) to the oscillating coil \( L_p \), but also acts as a transformer supplying high voltage. Various taps are attached to output coil \( L_e \) so that the output voltage may be adjusted so as not to overload the
FIGURE A3

HARTLEY TYPE PIEZOELECTRIC OSCILLATOR
FIGURE A4

REACTIVELY COUPLED PIEZOELECTRIC OSCILLATOR

[Diagram of a reactively coupled piezoelectric oscillator with labeled components such as L, C, and A.]
quartz. To avoid sparking at the quartz Q a safety spark F is put in parallel with it. In this circuit the generator is operated from the AC main, one phase only being used for the anode current. It is naturally preferable for energy reasons to put a steady direct voltage on the anode, and this may be obtained from a DC machine or from the alternating mains by means of a rectifier.

It is possible to use the quartz crystal as a control of the oscillation by controlling a valve at its own frequency, the valve then supplying the necessary alternating field for maintaining the crystal vibrations. This is achieved by connecting the quartz not in parallel to capacity as before but either between the grid and the anode or between the grid and the positive pole of the anode battery.

The placing of the quartz is of prime importance if the set is to operate properly. It is easily possible to break the quartz by improper support. Also the electrical connections must be such that the electric charge is evenly distributed over the face of the quartz crystal. Good contact can be secured by silvering the crystal face, taking care to get a uniform deposit (34). Proper electrodes and quartz supports are the most sensitive and difficult part of a piezoelectric generator.

**USES OF ULTRASONICS**

Ultrasonic waves have been used in many fields. The high frequency sound waves are a handy laboratory tool
in that they are comparatively easy to generate and use. Also there is scarcely any practical limit either as to the frequency range or the sound intensity. For example, Newton Gaines, {31}, describes the development of an oscillator capable of pushing the magnetostriction oscillations of nickel to the limit set by the mechanical strength of the tube. He calculated the tube was stressed to one half the elastic limit during normal operation. The tube would fail from fatigue after a run of about forty-five minutes at 8900 cycles/sec. The powerful electric pulses used would produce an amplitude of 0.01 millimeters with the tube in water. The tremendous forces employed can be seen by calculating the maximum acceleration on the tube. This is shown by:

\[ Y = 4\pi^2 n^2 A \quad (18) \]

\[ Y = \text{maximum acceleration, km/sec}^2 \]
\[ n = \text{frequency, cycles/sec.} \]
\[ A = \text{amplitude, km.} \]

Using the 8900 cycles/sec. and 0.01 mm. amplitude mentioned above, calculation shows the maximum acceleration to be 31 km./sec.\(^2\).

Piezoelectric crystals can also be used to produce intense high frequency waves. The necessity for careful mounting of the quartz crystal is indirectly shown by the following description of a quartz oscillator built and operated by R. W. Wood {82}. 
"We operated usually with voltages in the vicinity of 50,000 at frequencies ranging from 200,000 to 500,000. An enormous amount of energy was delivered with great acceleration of the quartz surface. The acceleration of a bullet in the barrel of a modern rifle is about 300 kilometers per second. Let us now calculate the acceleration of the surface of a quartz plate 2.87 mm. in thickness, when in resonant vibration. The frequency is one million and the distance traversed during each vibration is about 0.0008 mm. Its maximum velocity is about 5 meters per second, and as it acquires this velocity in one four millionth of a second, its average acceleration is about 20,000 km./sec.². Its maximum acceleration, or that which it has at the ends points of its to and fro path, would be 40,000 km./sec.². If a body moved off into space with that acceleration operating continuously, it would be a million miles away in ten seconds and would be traveling with a velocity greater than that of light."

Using these and similar instruments to produce ultrasonic waves, various researchers have investigated many possible uses of high frequency waves. Powerful sound oscillations will char and finally burn non-elastic materials such as cork and wood while setting up fatigue stresses in elastic materials such as metals and glass (31), (63). The rapidly alternating compression and tension set up by the sound waves can be used to kill bacteria, frogs, and fish. This led to a partially successful investigation of the possible use of ultrasonics in the continuous pasteurization of milk (31).

Perhaps the most dramatic and widespread use of ultrasonics has been in underwater signaling, detecting, and sounding. In such work a narrow beam of sound is often desirable. High frequency has a great advantage since the
narrowness of the beam depends on the radius of the vibrating plate as compared with the wave length of the radiated sound (11), (20). For a circular piston of radius, \( R \), the half apex angle of the cone, \( \theta \), within which almost all the sound is radiated, is given by the approximate formula:

\[
\sin \theta = 0.61 \frac{w}{R}
\]

(19)

\( w \) = wave length

Ultrasonics has found a further practical application in the testing of materials. Flaws and cracks in castings will reflect ultrasonic vibrations traveling through the casting. This reflection can be recognized and the defective casting discarded (11), (20). This procedure is a partial replacement for more tedious and expensive X-ray examination. A further application is the quick testing of metal thickness of tanks and other structures of plate metal (25). This permits safety inspection of acid tanks and other corrosion susceptible containers without having to empty the contents.

Stable liquid dispersions and colloidal solutions have been formed by high frequency waves (45), (68). While ultrasonics tend to promote the formation of hydrosols under certain conditions, (34), they have been widely used to coagulate aerosols (23), (24), (65). Smog and smoke particles are agglomerated and precipitated by passing the gas stream through an ultrasonic field.
The vibrations of a quartz crystal have also been used to run an exceedingly accurate clock (39). The resonant frequency of both magnetostriction and piezoelectric oscillators depends not only on their shape but also on their temperature. However, W. A. Marrison found a way to cut quartz crystals in such dimensions so as to have no significant temperature coefficient of vibration. Previously W. G. Cady had discovered a method of using a piezoelectric crystal as a regulator in an electric circuit. Using both ideas, Marrison produced a low frequency electric current of remarkably steady frequency. This is used to run a clock which is claimed to be by far the most accurate in existence. Its timing is so precise that the gravitational effect of the moon on swing pendulums has been determined.

Further investigations of ultrasonics include the degassing of liquids (11), (20), stream pollution (87), distillation (22), depolymerization (85), and chemical processing (11), (73), including the hydrogenation of coal (88). Ultrasonics have even been used in such practices as aging whiskey (90), and in washing clothes.
APPARATUS

The circuit used in this thesis was taken from that of a magnetostriction oscillator built by Newton Gaines (31). Various modifications were used as suggested in numerous articles on the general design of such an oscillator (11), (14), (30), (47), (51), (55). The apparatus is diagramed in Figures A5 and A6. The first gives chiefly the details of the electric circuit, while the second shows the dialysis cell itself. The component parts of the electric circuit are as follows:

RESISTORS

$R_1$ - A voltage divider across the 115 volt input to control the filament voltage of the power tube (805).

$R_2$ - A Variac type voltage divider to control the power tube plate voltage.

$R_3$ - A voltage divider used to control the current through electromagnet E1.

$R_4$ - 5000 ohm, 50 watt grid leak.

$R_5$ - 250,000 ohm, 50 watt condenser leak around variable condenser $C_1$. The high voltages used would cause $C_1$ to spark badly if a leak were not provided. $R_5$ could be removed if $C_1$ were so constructed that there would be no sparking.
FIGURE A6
APPARATUS DIALYSIS CELL

Cooling Water

Suction

Stirrer

Iron

L1

L2

N1

Solution
Membrane

Water

Approximately Half-Size
R₆ - A leak to discharge capacitors C₈ and C₉ when the set is turned off.

CAPACITORS

C₁ - 50 to 1500 mmfd., variable, 64 plate, air-gap condenser. This is the tuning condenser of the circuit which, together with inductance L₁, forms the oscillating circuit.

C₂, C₃, C₄, C₅ - Various fixed capacity condensers. These condensers are mounted in parallel with C₁ and so mounted that they may be switched in or out at will. This arrangement gives a very wide possible variation of capacity. In the apparatus the range is from 0.00005 mfd. to 0.01350 mfd. All these capacitors are rated at 5000 test volts and have the following capacities:

  C₂ - 0.001 mfd.
  C₃ - 0.002 mfd.
  C₄ - 0.003 mfd.
  C₅ - 0.006 mfd.

C₆ - 1 mfd., 3000 volt, fixed condenser. Being of much higher capacity than the condensers with which it is in series, this condenser does not affect appreciably the overall capacity of the circuit. Its function is to prevent overloading of ammeter Aₐ in case of sparking across C₁.
C_7 - 0.003 mfd., 5000 volt condenser placed in parallel to the grid leak R_4 in order to permit the fluctuating voltages from inductance L_2 to move freely to the power tube grid.

C_8, C_9 - 2 mfd., 3000 volt, fixed condensers. These are to filter the high voltage DC coming from the power supply.

**INDUCTANCES**

L_1 - This inductive coil forms, with C_1, the oscillation circuit. It is wound on a 1 inch O.D. Bakelite spool and composed of 600 turns of No. 22 B. and S. double cotton covered wire giving an inductance of approximately 0.012 henry.

L_2 - This is the grid feed-back inductance. Wound of 300 turns of wire on the same spool as L_1, its feed-back voltage to the grid is created by the mutual inductance of L_1 and L_2 through the vibrating rod Ni.

L_3, L_4 - High inductance filter coils for the power supply current.

**RECTIFIERS**

B_1 - Two diodes give full wave rectifications of the high voltage AC coming from transformer T_2.

B_2 - A 30 volt, 5 amp., full wave, selenium rectifier supplies the DC needed for electromagnet El.
TRANSFORMERS

$T_1$ - A step-down transformer to supply the power tube filament.

$T_2$ - A step-up transformer which, after rectification by $E_1$, supplies the high voltage for the power tube plate.

$T_3$ - A step-down transformer to supply the filaments of the rectifier tubes.

$T_4$ - A step-down transformer to reduce the AC voltage to the selenium rectifier $E_2$. The equipment used gave a 24 volt, 3 amp. output.

OTHER EQUIPMENT

El - An electromagnet. It is made of 1500 turns of No. 18 B. and S. double cotton covered copper wire wound on a 1 inch Bakelite spool. The magnet magnetizes the nickel tube and thereby increases its oscillations.

Iron - The iron core for electromagnet El.

Ni - The nickel, magnetostriction tube.

805 - The power tube. It requires a filament supply of 10 volts and will take 1500 volts maximum plate voltage.

OPERATION

In order to examine the operation of the electrical circuit it will be divided into four parts and each part
discussed separately. These parts are:

1. The high voltage supply.
2. The power tube filament supply.
3. The electromagnet supply.
4. The oscillating circuit itself.

THE HIGH VOLTAGE SUPPLY

Ordinary 115 volt AC is impressed across Variac $R_2$, transformed into high voltage AC by transformer $T_2$, and rectified by diodes $B_1$. The fluctuating DC voltage leaving $B_1$ is filtered through capacitors $C_8$ and $C_9$ while the fluctuating DC current is smoothed through inductances $L_3$ and $L_4$. Voltmeter $V_1$ and ammeter $A_{m_2}$, both DC instruments, measure the output voltage and current. Resistor $R_6$ provides a leak of considerably less resistance than $V_1$ through which $C_8$ and $C_9$ may discharge when the set is turned off.

THE POWER TUBE FILAMENT SUPPLY

The 115 volt AC is reduced somewhat by voltage divider $R_1$ and then further reduced to the desired value of 10 volts by transformer $T_1$. This voltage is measured by voltmeter $V_2$ and the current used to heat the power tube filament.

THE ELECTROMAGNET SUPPLY

Transformer $T_4$ takes the 115 volt AC input and supplies 24 volt AC to the full wave, selenium rectifier $B_2$. The fluctuating DC from $B_2$ is put across voltage divider $R_3$
and used to activate the electromagnet El. The electromagnet current is measured by DC ammeter Am$_3$ and is not filtered except for the filtering action of the magnet windings.

**THE OSCILLATING CIRCUIT**

The oscillating elements of the circuit are the inductance L$_1$ and the capacitor C$_1$, together with any of the parallel capacitors C$_2$, C$_3$, C$_4$, or C$_5$, which might be switched in. The oscillating current is measured by ammeter Am$_1$ and causes the magnetostrictive effect in the nickel tube Ni. This effect induces a voltage in inductance L$_2$, which voltage is applied to the grid of the vacuum tube 805. This grid voltage affects the plate voltage and thus provides the feedback needed to keep the oscillation going. This oscillation is strongest at the resonant frequency of the vibrating tube. The magnetic field through the iron core of electromagnet El keeps the section of the tube through L$_1$ and L$_2$ permanently magnetized.

**THE DIALYSIS CELL**

The construction of the dialysis cell is incompletely shown in Figure A5 which primarily covers the electric circuit. Figure A6 is more detailed as it shows the agitation and cooling devices omitted from the first drawing. The dialysis cell is composed essentially of two containers. The inner container holds a solution of sodium hydroxide and is merely a section of 90 mm Pyrex tubing. The solution in the inner container is separated from the water in the outer,
glass container by means of a Cellophane membrane stretched across the open end of the Pyrex tube. Both liquids are kept well mixed with stirrers in order to insure that all concentration gradients are across the membrane only and not partly across the membrane and partly in the bulk of the liquids. Ultrasonic vibrations are induced into the solution in the inner container by dipping one end of the vibrating tube into the liquid itself. This allows the sound waves to travel through the liquid and strike directly on the membrane below.

Since hysteresis losses cause the magnetostriction tube to heat up and eventually cease vibrating, the tube must be cooled continuously to achieve steady operation. This is accomplished by allowing cooling water to trickle down the inner wall of the tube. However, if an appreciable amount of water were to collect in the bottom of the tube, the vibrations would be increasingly damped. The water is therefore removed steadily through a suction tube which reaches into the tube itself. An aspirator is a convenient vacuum source.

The membrane material chosen for the experiments was Cellophane. Manufactured by the Du Pont Company, it is readily available, has very constant characteristics, has a reasonable dialysis coefficient, and is amply strong. The Cellophane used has a Du Pont classification of 450 PT. It is a plane, transparent Cellophane sheet 0.0013 inches thick with a yield point of 15,000 lb./in.². It is about one and
one half times as thick as the Cellophane ordinarily used for packaging foods, cigarettes, and the like. Also, it is of slightly different manufacture, passing water vapor at a higher rate than the "moisture-proof" Cellophane used for cigarettes.
EXPERIMENTAL PROCEDURE

The experimental procedure used is fairly simple. For a run the membrane to be used is firmly fixed over the end of the inner container. Then measured amounts of water and solution are introduced into the outer and inner containers respectively. The fluid levels in the two containers are adjusted to the same height so that there will be no pressure difference across the membrane. The stirrers and vibrator are then started and the set allowed to operate for ten minutes. This is to allow time for the establishment of the solute concentration gradient through the membrane. Two samples are taken for a zero reading and further single samples at definite time intervals throughout the run.

In a typical run 500 cc. of sodium hydroxide solution and 6500 cc. of water would be used. Time intervals are forty minutes for the first two hundred minutes and fifty minutes thereafter. Samples are 1 cc. These would be diluted with distilled water and titrated against sulfuric acid using phenolphthalein indicator. This determination of the change of normality of the solution in the inner container with time permits calculation of the rate of dialysis together with the membrane coefficient.
CALCULATIONS

For calculating purposes it was assumed that the dialysis followed the equation:

\[
\frac{dN}{d\theta} = KA \Delta X \tag{1}
\]

\[
\frac{dN}{d\theta} = \text{mass transfer rate, gm./min.}
\]

\[
K = \text{membrane coefficient, cm./min.}
\]

\[
A = \text{membrane area, cm.}^2
\]

\[
\Delta X = \text{concentration gradient driving force across the membrane, gm./cm.}^3
\]

Equation (1) follows the classic diffusion equation in form. The dialysis constant \(K\) is an overall coefficient and includes the effects of the liquid film on each membrane surface together with the membrane itself. In line with using an overall coefficient, the overall concentration difference \(\Delta X\) is also used.

Upon assuming that the vigorous stirring of each liquid insures complete mixing in the bulk of the liquid, the concentration gradient may be expressed in terms of the total weight of solute and total volume of liquid in each container.

\[
\frac{dN}{d\theta} = KA \left(\frac{N}{L_1} - \frac{N'}{L_2}\right) \tag{2}
\]

\[
L_1 = \text{liquid in inner container, cm.}^3
\]

\[
L_2 = \text{liquid in outer container, cm.}^3
\]

\[
N = \text{solute in } L_1, \text{ gm.}
\]

\[
N' = \text{solute in } L_2, \text{ gm.}
\]
The total solute in both $L_1$ and $L_2$ must equal the amount in the initial charge to the inner container.

$$N + N' = N_0$$

(3)

$N_0 =$ total solute introduced in original charge, gm.

Therefore:

$$\frac{dN}{d\theta} = KA \frac{N}{L_1} - \frac{N_0 - N}{L_2}$$

(4)

Which rearranges to:

$$\int_{N_1}^{N_2} \frac{dN}{(L_1 + L_2)N - L_1N_0} = KA \frac{\theta_2}{L_1L_2}$$

(5)

Equation (5) can be integrated assuming that the only variables are $N$ and $\theta$.

$$\ln \frac{(L_1 + L_2)N_1 - L_1N_0}{(L_1 + L_2)N_2 - L_1N_0} = KA\frac{L_1 + L_2}{L_1L_2} \Delta \theta$$

(6)

In the above equation it should be noted that the subscripts on $L_1$ and $L_2$ refer to the volume of liquid in the inner and outer containers respectively. Conversely the subscripts on $N_0$, $N_1$, and $N_2$—all refer to the weight of solute in the inner container at various times.

For the ordinary run data is taken showing the variation of $N$ with $\theta$ with known $A$, $L_1$, and $L_2$. The value of $K$ is desired. Equation (6) may be arranged to solve for any unknown. To find $K$: 
$$K = \frac{L_1 L_2}{A(L_1 + L_2) \Delta \theta} \ln \frac{(L_1 + L_2) N_1 - L_1 N_0}{(L_1 + L_2) N_2 - L_1 N_0}$$

(7)

In this form the membrane coefficient for one or more of any time intervals in a series can be found.

When the dialysis coefficient for a run has been determined, it is possible to check the agreement between experimental and calculated mass transfer rates. This is done by solving for $N_2$ at various times assuming constant coefficient $K$.

$$N_2 = \frac{(L_1 + L_2) N_1 - L_1 N_0}{(L_1 + L_2) \Delta \theta} + \frac{L_1 N_0}{L_1 + L_2}$$

(20)
ACCURACY

The accuracy of the results obtained depends on the validity of the assumption used in the integration of the dialysis rate equation together with the necessity of obtaining and correctly titrating representative samples. The assumptions made in integrating the rate equation include complete mixing of both liquids at all times, constant membrane area and dialysis coefficient, and constant liquid volumes on both sides of the membrane.

The liquids in both containers were stirred vigorously throughout all runs. This should insure complete mixing and all pertinent data justify that assumption. Two samples were taken from different parts of the sodium hydroxide solution for the zero point of each run. This served as a check for accuracy in the determination of this most important point for calculations and also as a check for complete mixing in the solution. Any difference between the two samples would be a combination of mixing in the solution, sampling, and titration. In no case, however, did the samples show a concentration difference greater than one percent and usually the difference was considerably less. This negligible difference between simultaneous samples was found by double sampling both during and at the end of various runs. It is safe, therefore, to assume not only complete mixing in the liquids, but also adequate accuracy in sampling and titration.
The assumption of constant membrane area is undoubtedly well justified while constant dialysis coefficient is indicated by the generally good agreement of experimental mass transfer rates with rate calculated using a constant coefficient. The experimental and calculated transfer rates are listed in the data sheets at the end of this thesis together with plots of the same data for Runs 2 through 9.

At first glance the assumption of constant liquid volumes seems well taken. However, the liquid volumes did vary during a run due to evaporation losses and sampling. Calculations show that these losses have only slight effects and therefore can be neglected. Measurements of liquid volumes after a run showed that evaporation amounted to less than two percent of either liquid in all cases. In addition this small error is largely canceled out since evaporation from one liquid tends to be counterbalanced by evaporation from the other. That is the concentrating effect of evaporation in one liquid is countered by the concentrating effect in the other and the concentration gradient tends to be preserved on a higher level.

Each of the periodic samples taken during a run was only one cubic centimeter. This was to minimize the effect of taking periodic samples. Over a 300 minute run, starting with 500 cc. in the inner container, the ten samples taken amount to 2% of the liquid bulk. The error introduced is, however, not of the order of 2% but something less than 0.5%.
This reduction comes from the fact that the solute and solvent are, of course, removed together in the sample. Therefore, the proportions removed throughout the run are very nearly the same as the proportions remaining. The simplified calculations that result from assuming constant liquid volumes justifies ignoring the slight error involved. The following calculation does not show the error incurred during a typical run but does show the maximum possible error due to samples. The first calculation is for the ideal case of no samples during the run while the second gives the maximum error by assuming all samples were taken at the start of the run. The actual error should be less than half the maximum error.

**ERROR FROM SAMPLES**

Let \( K = 0.0280 \text{ cm.}/\text{min.} \)

\[ A = 100 \text{ cm.}^2 \]

\[ L_1 = 500 \text{ cm.}^3 \]

\[ L_2 = 6500 \text{ cm.}^3 \]

\[ \theta = 300 \text{ min.} \]

\[ N_0 = 20 \text{ gm.} \]

\[ N_1 = 19 \text{ gm.} \]

\[
N_2 = \frac{(L_1 + L_2) N_0 - L_1 N_0}{K A (L_1 + L_2) \Delta \theta} + \frac{L_1 N_0}{L_1 + L_2} \quad (20)
\]
Assume no samples during run:

\[ N_2 = \frac{(7000)(19)-(500)(20)}{1000} + \frac{(500)(20)}{7000} \]

\[ N_2 = \frac{17.5714}{6.1057} + 1.4286 \]

\[ N_2 = 4.307 \text{ gm.} \]

\[ M = 0.2153 \text{ mol/lit.} \]

Assume all 10 cc. of sample out at start of run:

\[ N_2 = \frac{(6990)(19)-(490)(20)}{6990} + \frac{(490)(20)}{6990} \]

\[ N_2 = \frac{17.528}{6.3185} + 1.402 \]

\[ N_2 = 4.187 \text{ gm.} \]

\[ M = 0.2136 \text{ mol/lit.} \]

Maximum % error = \[ \frac{0.2153-0.2136}{0.2153} = 0.790\% \]

**STANDARD SOLUTIONS**

The same procedure was used in making all acid and base standard solutions. The primary standard was crystals of potassium acid phthalate. These were weighed on an analytical balance and dissolved in distilled water. The normality of a basic solution was found by titration against these weighed standards. Acid solutions were standardized by titration against previously standardized basic solutions. The indicator used was an alcohol solution of phenolphthalein. In all titrations the end point was taken at a faint pink color.
REPRODUCIBILITY

Reasonable care in operating the apparatus will give readily reproducible results, especially without sound waves. The close agreement of the dialysis coefficients obtained in runs 2, 3, 4, 6, 7, 12, 15, and 24, all without sound, show that consistent results can be achieved. The same consistent results should be attained in those runs using sound waves provided the nickel tube is maintained at its resonant frequency. The input power and frequency of the electric circuit can be closely controlled but this is no guarantee that the sound intensity will be equally constant. The chief danger is that the tube will change its temperature and thereby alter its resonant frequency. This would greatly reduce the sound power output as intensity falls off rapidly as the impressed frequency departs from the resonant frequency. This is shown by the equation:

\[
\frac{W}{W_{\text{max}}} = \frac{4k^2p^2}{(n^2-p^2)^2 + 4k^2p^2}
\]

\[
(10)
\]

\[
W = \text{power output}
\]

\[
W_{\text{max}} = \text{maximum power output at resonance}
\]

\[
k = \text{damping constant}
\]

\[
n = \text{resonant frequency}
\]

\[
p = \text{forced frequency.}
\]

As can be seen, at low damping the power change through resonance will be abrupt. Therefore the necessity of maintaining resonant vibrations becomes clear. This is achieved by
holding the tube at constant temperature. This is especially true for nickel oscillators as nickel has a comparatively high coefficient of frequency change with temperature. Constant temperature is maintained by adequate cooling and the cooling device used in this thesis appeared to be sufficient provided there is a steady flow of water.

Two sets of duplicate runs were made to test reproducibility while using sound. Runs 9 and 11 were made at 10,900 cycles/sec. and 25 watts electric power input. The dialysis coefficients obtained, 0.0301 and 0.0302 cm./min. respectively, agree to within 0.33%, which is the range of agreement of the non-oscillating runs. The other pair of duplicate runs, 28 and 29, were made at 14,000 cycles/sec. and 50 watts input. The coefficients for these runs, 0.0332 and 0.0328, agree to within 1.21%.
DATA SHEETS

The following pages present the original data sheets together with calculated values of the various operating quantities and plots of several runs. Table AI lists the operating variables for all runs. This information includes:

- Run Number - From 2 to 32
- Membrane Area - Always 56.7 cm²
- Membrane Used - A, B, C, D, or E
- Liquid Quantities - \( L_1 \) and \( L_2 \), cm³
- Solution Concentration, M - Moles per liter of solution
- Run Length, G - Minutes
- Mass Transferred \( \Delta N \) - Total grams transferred in time, G
- Membrane Coefficient - K
- Magnetostriction Tube Used - Nickel tube 2, 3, 4, 5 or 6
- Frequency, f - Cycles/second
- Electric Power Input, W - Watts
- % Increase of dialysis constant over base rate.

The plots located after Table AI are graphic presentations of the results of runs 2 through 9. Each run is presented in three plots. The first shows the relation of time and total mass transfer across the membrane. As would be expected, all these plots show the rate of mass transfer decreasing with increasing time. The second plot is a graphical representation of equation (6):
\[
\ln \frac{(L_1 + L_2) N_1 - L_1 N_0}{(L_1 + L_2) N_2 - L_1 N_0} = \frac{KA (L_1 + L_2)}{L_1 L_2} \Delta \theta
\]  

(6)

A plot of the logarithmic term against time should give a straight line through the origin with slope equal to \(KA (L_1 + L_2)/L_1 L_2\). Knowing the values of all quantities in the slope except for the dialysis coefficient, \(K\), it is easy to determine the dialysis coefficient for the run in question. The third plot shows transfer rate against time. Both experimental and calculated transfer rates are plotted so that a comparison may be made. The dialysis coefficient, as determined by equation (7), are used to obtain the calculated values.

The data sheets contain all information pertinent to every run. The values calculated and shown for runs 2 through 9 in the plots have been calculated for all runs and are listed in the data sheets. The sheets first give the preliminary data given in Table \(A1\). The additional information includes:

- \(\theta\), Min - Time intervals at which data was taken.
- M, Mole/Liter - Solution concentration at the several sample times.
- N, GM - Weight of NaOH corresponding to measured solution concentration.
  
  \(N = N_0 \text{ at } \theta = 0\).
$\Delta N$, GM - Weight of NaOH transferred across membrane since last measuring time.

$\Sigma \Delta N$, GM - Total weight of NaOH transferred across membrane since start of run.

Log Term - Calculated value for use in equation (6).

$K_{per}$, CM/Min. - Dialysis coefficient for any one measuring time interval.

$K_{ov}$, CM/Min. - Overall dialysis coefficient since start of run.

$\Theta$, Min. - Mid-points of the several measuring intervals.

$dN/d\Theta$, GM/Min. - Calculated and experimental mass transfer rates.
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<th>$L_2$ Min.</th>
<th>$\Theta$ CM</th>
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Run 2  
Time vs Mass Transferred
Mem C

\[ N_1 - N_2 \text{ g.m.} \]
Run 3
Mem B

Time vs Mass Transfered

\[ N_1 - N_2 \text{ g/m} \]
Run 3: $K = \frac{K_2 + L_2}{L_1 + L_2} = 0.00339$

$K = 0.0279$ cm/mm

\[ \frac{\text{OD} (L_1 + L_2) N}{L_1 + L_2} \]
Run 4
Slope = \frac{K_A(L_1 + L_2)}{L_1 L_2} = 0.00266

K = 0.0280 \text{ \textdegree/min}
Run 5
Slope = \frac{KA(L_1 + L_2)}{L_1 L_2} = 0.00433
\[ K = 0.0352 \text{ cm/min} \]
Run 6
\[ \text{Slope} = \frac{KA(L_1 + L_2)}{L_1 L_2} = 0.00343 \]
\[ K = 0.0281 \text{ cm}^2/\text{min} \]
Run 7

\[
\text{Slope} = \frac{K_A(L_1 + L_2)}{L_1 L_2} = 0.00342
\]

\[
K = 0.0280 \text{ cm}^3/\text{min}
\]
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