Effect of the Resonance Parameter on a Chemical Reaction Subjected to Ultrasonic Waves

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Experimental results are presented which indicate that the application of a fixed intensity of ultrasonic waves to a water-tetrachloride solution containing dissolved air provides yields of chlorine varying from zero to maximum simply as a function of the liquid height in the capillary above the transducer. The difference in heights of the liquid between zero and maximum yields is found to be equal to one-quarter the wavelength of the ultrasonic wave in the liquid. A mathematical model to explain this phenomenon is presented.

The chemical reaction effects of ultrasonics have been extensively studied during the past three decades. During this time, a large amount of data has been accumulated (*1*); however, it has only been in the past ten years that a reasonable explanation has been proposed. Researchers in the field have generally agreed that acoustical cavitation is necessary before any chemical reaction effect due to the application of ultrasonic waves can be observed. The most recent theory (*2* to *6*) suggests that small dissolved gas bubbles, microscopic dust particles, or discontinuities in a liquid may act as nuclei for cavitation to begin. During the rarefaction portion of the sound wave, these small bubbles will expand. Conversely, during the compression portion of the sound wave, the expanded bubbles will again collapse to very small volumes. If this volume change occurs adiabatically, the temperature attained in the collapsing bubbles may be as high as 10,000°K. (*3*). This high temperature theoretically accounts for the chemical reaction effects which have been observed with the application of ultrasonic waves.

Since so many variables can affect the reproducibility of chemical reaction yields when subjected to ultrasonic waves, it has been very difficult for any one investigator to reproduce the results of another investigator. In fact, each investigator has generally not been able to expect reproducibilities better than 10% in his own work. It is the purpose of this work to show that the height of the liquid level above the ultrasonic source is a critical parameter and that a change in this height by as little as 2 mm. can result in a chemical yield which varies from zero to a maximum. This critical parameter is termed the *resonance parameter*. The exact distance is a function of the specific reaction and the frequency of the transducer.

THEORETICAL CONSIDERATIONS

Noltingk and Neppiras (*3, 4*) have shown that to have acoustical cavitation the pressure amplitude of the sound wave must exceed some critical value which they called the *cavitation threshold*. In addition, they showed that the intensity of cavitation increased with an increase in pressure amplitude of the sound wave when all other parameters were held constant. Since the yield of a chemical reaction subjected to ultrasonic waves is directly proportional to the intensity of cavitation and the cavitation intensity is proportional to the pressure amplitude of the sound wave, the chemical yield is therefore proportional to the pressure amplitude of the sound wave.

In this study it is of interest to determine how the pressure amplitude of a sound wave in a liquid changes as the height of the liquid above the transducer is varied. This specific arrangement is shown in Figure 1 where a column of liquid of height h is subjected to ultrasonic waves from the transducer. The pressure variation of a sound wave traveling in a medium is given by (*7*)

$$p_x = Pe^{-\alpha x}e^{i(\omega t - kh)} \qquad (1)$$

For simplicity, let the solid transducer at $x = 0$ be vibrating with an infinitely small amplitude and the pressure vibrations of the face of the transducer be changing by (*8*)

$$p_{x=0} = Pe^{i\omega t}$$

To account for energy losses of the sound wave as it is reflected at the two boundaries, $x = 0$ and $x = h$, the

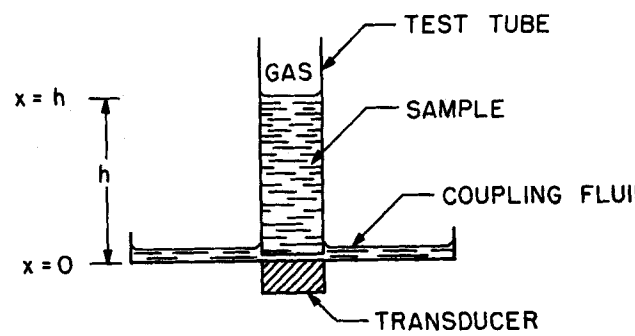

Fig. 1. Simplified sketch of equipment arrangement.

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reflected wave can be multiplied by a reflection coefficient (8). Let the reflection coefficient at $x = 0$ be σ and at $x = h$ be β.

After a time t has elapsed, the acoustical pressure at a point x in the column is represented by a summation of terms, including a term due to the pressure wave propagated directly from the ultrasonic source and terms due to the pressure wave propagated originally from the ultrasonic source but reflected any number of times by the two fixed boundaries at $x = h$ and $x = 0$. Each wave upon reflection at $x = h$ will undergo a phase change of 180 deg. because of the large differences in acoustical densities between the liquid and gas phases (9). However, upon reflection from the liquid-solid interface at $x = 0$ there is no phase change of the sound wave. The pressure at any point x can then be represented as (7)

$$p_x = Pe^{i\omega t}\left[e^{-(\alpha+ik)x} + \beta e^{-(\alpha+ik)(2h-x)} + \beta^2\sigma e^{-(\alpha+ik)(4h-x)} + \beta_2\sigma e^{-(\alpha+ik)(4h-x)} + \ldots\ldots\ldots\ldots\ldots\ldots\right] \quad (3)$$

If the liquid in the column is water, the attenuation coefficient is approximately zero. Since the acoustical impedance of the water is much greater than the acoustical impedance of the air, the reflection coefficient β at the gas-liquid interface is approximately minus one. Equation (3) now takes the form

$$p_x = Pe^{i\omega t}\left[\frac{e^{-ikx} - e^{-ik(2h-x)}}{1 + \sigma e^{-ik2h}}\right] \quad (4)$$

Consider now the pressure at the points given by $x = n\lambda/2$ where n is a whole integer and λ is the wavelength. Equation (4) becomes

$$p_{x=n\lambda/2} = Pe^{i\omega t}\left[\frac{1 - e^{-i2kh}}{1 + \sigma e^{-i2kh}}\right] \quad (5)$$

Equation (5) can also be written in terms of the sine and cosine functions. If the resulting equation is normalized, Equation (5) becomes

$$p_{x=n\lambda/2} = Pe^{i\omega t}\left|\frac{(1-\sigma)(1-\cos 2kh) + i(1+\sigma)\sin 2kh}{1 + \sigma^2 + 2\sigma\cos 2kh}\right| \quad (6)$$

The magnitude of the pressure amplitude at $x = n\lambda/2$ is given by

$$\overline{P}_{x=n\lambda/2} = P\left|\frac{[(1-\sigma)^2(1-\cos 2kh)^2 + (1+\sigma)^2\sin^2 2kh]^{1/2}}{1 + \sigma^2 + 2\sigma\cos 2kh}\right| \quad (7)$$

For the case where there is 100% reflection at the liquid-solid interface, $\sigma = 1$ and Equation (7) becomes

$$\overline{P}_{x=n\lambda/2} = P\left|\frac{\sin 2kh}{1 + \cos 2kh}\right| \quad (8)$$

At points where cos $2kh$ equals minus one, Equation (8) is undefined. This occurs at values of h where

$$h = (2n+1)\lambda/4, \quad n = 0, 1, 2, 3 \ldots\ldots \quad (9)$$

that is, at $\lambda/2$ intervals. As $h \to (2n+1)\lambda/4$, $\overline{P}_{x=n\lambda/2} \to \infty$ by L'Hospital's rule. This indicates that at resonance ($\lambda/2$ intervals) and if there is 100% reflection at both interfaces in the liquid column, the pressure amplitude of the sound wave is infinite. At points where $h = (n+1)\lambda/2$ the pressure amplitude as given by Equation (7) is zero. Figure 2 shows the relation between the pressure amplitude and the height of liquid above the transducer as calculated from Equation (7) for an attenuation coefficient of zero and various values of reflection coefficient at the liquid-solid interface. For general application, both the ordinate and abscissa have been reduced to dimensionless quantities. Note, that for all three curves shown the pressure amplitude of the sound wave varies from zero to a maximum and back to zero as the height of the liquid level above the transducer changes by $\lambda/2$. From the work of Noltingk and Neppiras it can be expected that the cavitation intensity will change in the same manner as the pressure amplitude of the sound wave, and hence the yield of a chemical reaction due to cavitation should change in a similar manner.

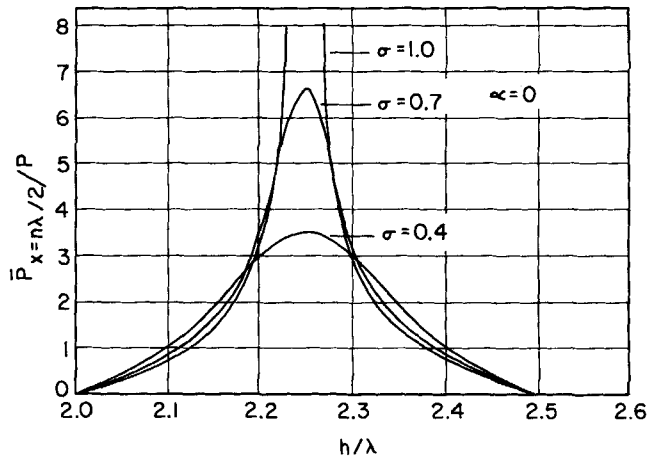

Fig. 2. Theoretical relation between the pressure amplitude of the sound wave and the height of liquid above the transducer ($2\lambda \leq h \leq 2.5\lambda$).

Equation (7) indicates that there is a direct proportionality between the pressure amplitude of the ultrasonic wave in the liquid P_x and the pressure amplitude at the transducer surface P. The latter is, in turn, proportional to the electrical power input to the transducer. Thus Equation (7) can be rewritten in the form

$$\overline{P}_{x=n\lambda/2} = cP_o\left|\frac{[(1-\sigma)^2(1-\cos 2kh)^2 + (1+\sigma)^2\sin 2kh]^{1/2}}{1 + \sigma^2 + 2\sigma\cos 2kh}\right| \quad (10)$$

The effect of changing the pressure amplitude at the transducer by a factor of three is shown in Figure 3 for an attenuation coefficient of zero and a reflection coefficient at the liquid-solid interface of 0.4. Again, the yield of a chemical reaction as a result of the application of ultrasonic waves should be proportional to the pressure amplitude at the transducer.

TEST REACTION

The reaction used in this study involved the liberation of chlorine from water, saturated with carbon tetrachloride and containing dissolved air. Weissler (*1, 11* to *13*) and Griffing (*14*) have performed extensive work on this specific reaction and Weissler has postulated the following mechanism:

$$CCl_4 + H_2O \rightarrow Cl_2 + CO + 2HCl$$
$$H_2O \rightarrow [O] + OH$$
$$2HCl + [O] \rightarrow Cl_2 + H_2O$$

This reaction proceeds only with the application of ultrasonic waves (*11*) and does not depend upon the oxygen in the dissolved air for the oxidation of the HCl to Cl_2, since it has been shown that the same reaction will occur if the dissolved gas is He, N_2, O_2, Ne, Ar, or Xe (*14*).

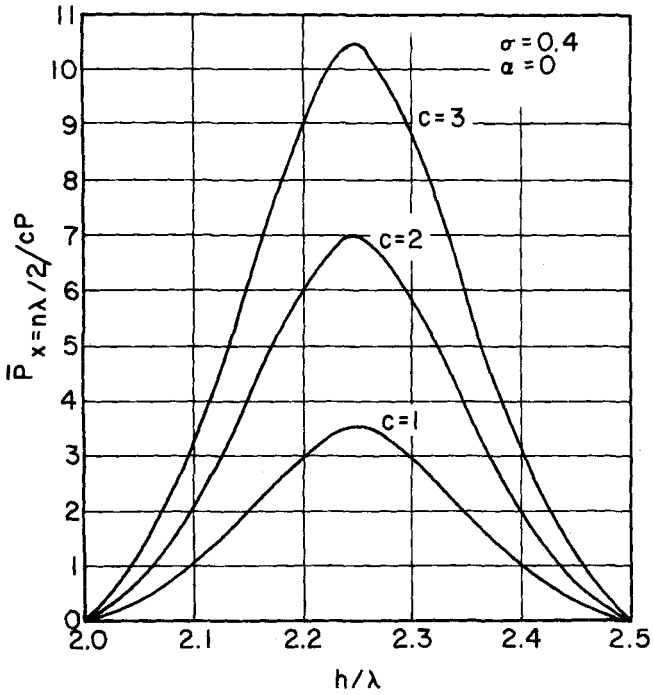

Fig. 3. Effect of changing the pressure amplitude at the transducer on the pressure amplitude of the sound wave in the liquid as a function of the liquid height above the transducer.

For the purposes of this study, it is not necessary to consider this reaction in any greater detail. When the pressure amplitude of the sound wave reaches the cavitation threshold, cavitation is initiated and chlorine is liberated.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A block diagram of the electronic circuit used in the experimental portion of this study is shown in Figure 4. A sinusoidal signal from the oscillator upon amplification was used to drive a transducer to produce the desired pressure amplitude. Power to the 115 kcs transducer was monitored by current and voltage probes attached to the cable leading to the transducer. The phase relationship between the two was observed with an oscilloscope. Further details of the electronic equipment are given elsewhere (*10*).

A simplified arrangement of the remaining equipment is depicted in Figure 1. A 1½-in. O.D. Pyrex test tube with a 2-mm. wall and a flat 1-mm. bottom was used to hold the water-carbon tetrachloride solution. This test tube was securely positioned ½ mm. above a stainless steel tray. The transducer in turn was carefully epoxied on the lower side of this same steel tray. Water in the tray was used as the coupling fluid between the transducer and the water-carbon tetrachloride solution. Great care was exercised to maintain a constant height of the coupling fluid. The liquid level h in the test tube (above the stainless steel tray reference point) was measured for each run by a high precision cathetometer.

An experimental run consisted of applying ultrasonic waves to a known amount of water-carbon tetrachloride solution for a specified length of time, noting the liquid level in the test tube during the run and then analyzing analytically for the amount of chlorine liberated. The analytical procedure involved the removal of 20 ml. of reacted sample from the test tube and mixing this with 20 ml. of a 0.5 N potassium iodide solution. This mixture was allowed to stand for 10 min. after the addition of 2 ml. of starch indicator. At the end of this time the mixture was titrated with 0.001 N sodium thiosulfate. The titration, which indicates the amount of iodine liberated from the potassium iodide as a result of oxidation by the chlorine, provides an indirect but effective method for determining the amount of chlorine formed during the application of the ultrasonic waves.

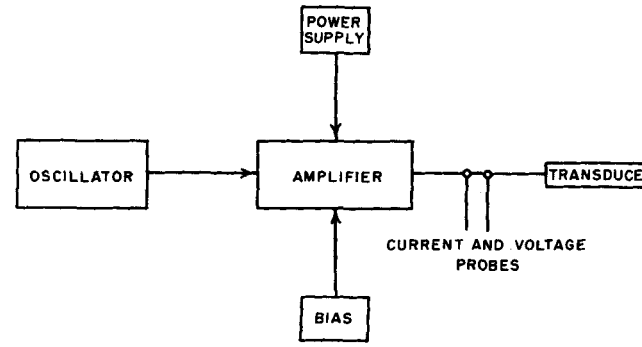

Fig. 4. Block diagram of the electronics circuit of the ultrasonic generator.

RESULTS AND DISCUSSION

Figure 5 shows the experimental yield of chlorine as a function of solution height above the transducer for a power input to the transducer of 2 w. For a frequency of 115 kcs, the wavelength in the water-carbon tetrachloride solution is 1.23 cm. Thus for a height of 2.46 cm. or 2λ, Equation (7) indicates that the pressure amplitude of the sound wave is zero. With zero pressure amplitude the corresponding chemical yield of chlorine would also be expected to be zero. This is verified experimentally.

Even though there is some scatter of experimental data, it is clear that as $h \rightarrow (2n + 1)\lambda/4$ equivalent to $9\lambda/4$ or 2.77 cm. that the yield of chlorine approaches a maximum. As noted earlier, this is predicted by Equation (7). As the height of liquid above the transducer is increased, the chemical yield of chlorine again decreases and reaches zero at a height of approximately 3.08 cm., which is equivalent to $5\lambda/2$. Again this follows the prediction of Equation (7). In a similar manner, increasing the height of the liquid above the transducer still further shows the same yield characteristics; that is, the chemical yield of chlorine increases from zero at a liquid height of $5\lambda/2$, increases to a maximum at a liquid height of $11\lambda/4$, and then decreases again to zero at a liquid height of 3λ or 3.69 cm.

The chemical yield of chlorine was also observed under carefully controlled conditions as a function of various measured power inputs to the transducer. Figure 6 shows the results for power inputs of 1.13, 1.8, and 4.34 w. for a change in liquid height above the transducer ranging from 2λ to $5\lambda/2$. The resulting curves show a remarkable similarity to the predicted pressure amplitude curves shown in Figure 3. At low values of power input to the transducer, the experimental points fall very close to the curve but as the power input is increased, scatter of experimental points becomes quite evident. This scatter

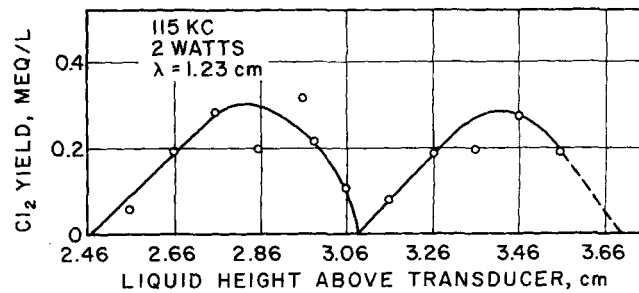

Fig. 5. Chemical yield of chlorine from a water-carbon tetrachloride solution as a function of the liquid height above the transducer.

can probably be explained by the vibrations of the liquid surface which were observed at the higher input powers. These surface vibrations most likely disturbed the reflection characteristics of the liquid-gas interface. Unfortunately, these vibrations appeared to be random and no correlation for their occurrence was found. The cause for these random surface vibrations is not known at this time.

The data in Figure 6 again justify, within experimental error, the mathematical model described earlier. First of all, zero chemical yield of chlorine (with one exception) was obtained for liquid heights of 2λ and $5\lambda/2$, while maximum yield for all power inputs to the transducer occurs at a liquid height of $9\lambda/4$ above the transducer. This is in agreement with Equation (7) and the experimental results shown in Figure 5. In addition, Equation (7) predicts that the chemical yield should be proportional to the pressure amplitude at the transducer. If the maximum chemical yields at the three power inputs to the transducer are compared, it is noted that (based on the lowest power input) the predicted maximum yields should, therefore, be in a ratio of 1.7 : 2.7 : 6.5. As noted from Figure 6, the experimental ratio is 1.7 : 3.1 : 5.6, indicating approximately a 15% discrepancy between the theoretical and experimental values. This is not unrealistic in view of the estimated 15% error in the combined measuring and analytical procedure followed during the course of the experimental work. To reduce this error, it will be necessary to devise a more direct approach for the analytical procedure.

Actually, a more quantitive comparison between theory and experiment is not possible at this time since the necessary measurements cannot be made. There is no known way of measuring effectively the pressure amplitude of a sound wave in a cavitating liquid since cavitation affects all measuring devices. Even if the pressure amplitude of the sound wave in the liquid could be ascertained, there is no way of calculating the possible yield of the reaction corresponding to a given pressure amplitude in the liquid, since this would involve a knowledge not only of the number of cavitation bubbles present at any given time, but also the temperature in each bubble and the reaction products in each bubble. Since these bubbles usually have radii on the order of 10^{-4} cm. (3, 4), it is impossible with present equipment to obtain the necessary measurements to make realistic calculations.

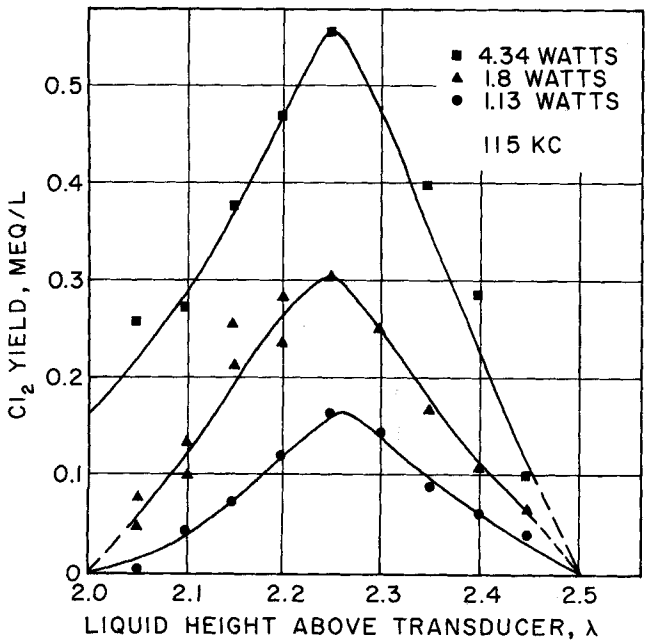

Fig. 6. Chemical yield of chlorine from a water-carbon tetrachloride solution as a function of the liquid height above the transducer for different input powers to the transducer.

CONCLUSIONS

This study provides both a mathematical model and experimental results to show that the parameter of liquid height on a chemical reaction subjected to ultrasonic waves is important. Specifically, the chemical yield of chlorine from a water-carbon tetrachloride solution is shown to vary from zero to maximum and back to zero as the liquid level of the solution is varied over intervals of one-half wavelength of the ultrasonic wave in the liquid. At 115 kcs this is equivalent to 0.61 cm. Since at higher frequencies this distance is even less, the liquid height above the transducer becomes an important factor in obtaining reproducibility of results whenever studies of chemical reactions are made in equipment similar to that shown in Figure 1.

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NOTATION

c = any constant greater than zero
h = height of liquid level above transducer, cm.
k = wave number, $2\pi/\lambda$, 1/cm.
p_x = acoustical pressure at distance x from transducer, atm.
P = pressure amplitude at the transducer, atm.
P_x = pressure amplitude in the liquid at height x, atm.
P_o = some arbitrary pressure amplitude at the transducer, atm.
t = time, sec.
x = distance from transducer, cm.
α = attenuation coefficient, nepers/cm.
ω = angular frequency, rad./sec.
λ = wavelength, cm.

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