

Invited Review

Second-Order Sonochemical Phenomena—Extensions of Previous Work and Applications in Industrial Processing

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Abstract

The first-order properties of acoustic waves (i.e., the to and fro particle displacement and velocity) can produce a number of second-order phenomena: cavitation, acoustic streaming, surface instability and radiation pressure. The dependence of cavitation induced phenomena (erosion, luminescence, chemical reactions) on the physical and acoustical parameters of a system are discussed. Some of the past work carried out in this field is analyzed and reinterpreted. In the light of this, it appears that the extent of the solubility of a gas has a pronounced effect on cavitation related phenomena in addition to the effect of other variables such as the ambient liquid temperature, the hydrostatic pressure, the specific heat ratio, the thermal conductivity of dissolved gas and the intensity and frequency of acoustic field. A summary of the application of sonic and ultrasonic energy to industrial processing operations is also provided. This discussion includes how the other second-order effects (e.g., interfacial instability) are related to the enhancement of these operations. The wide variety of processes in which the applications of acoustic energy has a beneficial effect suggests the versatility and broad commercial potential of sonochemical engineering.

1. INTRODUCTION

Traditionally, one is always looking for ways and means of increasing the quality of various industrial products and increasing the efficiency of the processing operation. In a wide variety of applications, a means of achieving this goal is by the application of acoustic waves to the processing system. Sonochemical engineer-

ing is the field-involving application of sonic and ultrasonic waves to chemical processing.

With the advent of many newer, higher intensity ultrasonic generators, acoustic waves are becoming ever more successful in enhancing chemical processing operations by increasing the rates of the individual transport phenomena involved in the overall operation. The mechanisms responsible for the observed increases in rates in transport and unit operations processes can be divided into two categories: *first-order effects* of fluid particles (displacement, velocity, and acceleration), and *second-order effects or phenomena* (radiation pressure, cavitation, acoustic streaming, and interfacial instabilities). Usually, it is one or more of the second-order effects which are responsible for the enhancements in the transport process. For an even greater use to be made of sonochemical processing on an industrial level, more research needs to be carried out to delineate the mechanisms producing the increased rate in a given system.

In the review that follows, we shall be principally concerned with acoustically induced cavitation and three cavitation related phenomena: erosion, luminescence and acceleration of chemical reactions. We shall first try to delineate the effect of the acoustical parameters and the properties of the liquid and gas on these three cavitation related phenomena. In addition, we shall offer alternative explanations (which are perhaps more plausible) for some of the experimental observations previously reported.

2. CAVITATION PHENOMENA

Cavitation is a three-step process consisting of nucleation, growth and collapse of a gas or vapor filled bubble in a body of liquid. The cavitation threshold for *homogeneous* liquids is of the order of hundreds of

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TABLE 1

The effect of physical parameters on cavitation

No	Independent variable	Dependent variable	Effects
A	Nature of liquid	Compressibility of liquid Surface tension Gas solubility Type of active intermediates/ radicals formed	Gas bubble dynamics Size of smallest nuclei Number of cavitation events, gas content Nature of chemical reaction
B	Pretreatment of liquid	Size distribution of cavitation nuclei	Cavitation threshold
C	Nature of gas	Gas solubility	Number of cavitation events, gas content
D	Static pressure	Specific heat, thermal diffusivity Size distribution of cavitation nuclei, gas solubility impedance of liquid	Intensity of cavitation events Number of cavitation events, cavi- tation threshold, velocity of bubble collapse, efficiency of energy transfer
E	Ambient liquid temperature	Gas solubility, liquid vapor pressure Sound wave length	Gas content of bubbles, cavitation intensity Resonance conditions
F	Acoustic intensity	Size of cavitation zone	Probability of cavitation events per unit volume
G	Acoustic frequency	Half period of collapse	Resonant bubble radius, probability of cavitation events per unit time
H	Time of irradiation	Total energy input	Extent of reaction, heat dissipation

atmospheres. The cavitation threshold of CCl_4 is, for example, reported to be 265 atm¹. The presence of microparticles, dissolved gas or other cavitation nuclei considerably reduce the liquid strength by acting as weak spots as evidenced by Briggs *et al.*², who were able to cavitate CCl_4 at an acoustic pressure amplitude of only 1.75 atm. For a given nuclei size distribution it is the acoustic parameters that determine what fraction of cavitation bubbles will behave as oscillating bubbles and what fraction will be transient cavities. The transient cavities are primarily responsible for the cavitation effects of erosion, luminescence, and sonochemical reactions. The observed macroscopic effect will be a combination of an *extensive* factor (size and number of bubbles) and an *intensive* factor (intensity of collapse)—the two not being necessarily independent of each other. Table 1 summarizes the most important factors thought to affect cavitation which we shall discuss in more details below.

A. Nature of liquid

The most common liquid used for ultrasonic cavitation studies is water as it is a very good solvent for gases

and other solutes. Yeager and co-workers,³ using isotopic exchange techniques, were able to establish that the water vapor molecules in a cavitation bubble were dissociated into atomic (H) and (OH) radicals. These radicals serve as initiators of various chemical reactions such as:

- the formation of H_2O_2 ⁴⁻⁶
- The liberation of Cl_2 from a saturated water- CCl_4 solution^{6,7}
- The oxidation of KI to give iodine⁸

There are other examples of ultrasonically induced chemical reactions between two dissolved gases in an aqueous medium in which the dissociation of H_2O does not seem to play an important role. For example, molecules of N_2 and O_2 dissolved in water combine to form oxides of nitrogen⁹. If the water is saturated with N_2 , H_2 ammonia is formed¹⁰. A mixture of N_2 , H_2 and CO can lead to formation of HCN and HCOOH ¹¹.

Although water is the primary solvent used in sonochemical studies so far, it has been shown that cavitation also occurs in organic liquids (benzene, acetone,

etc.) leading to depolymerization of polyvinylacetate, nitrocellulose and other polymers¹².

The presence of "dissolved impurities" in a liquid affect cavitation phenomena. Negishi¹³ found that the relative sonoluminescence intensity of aqueous solutions of some electrolytes (Na₂CO₃, NaCl, Na₂S₂O₃, and NaNO₃) was a factor of 1.5 to 4 greater than that of tap water. The presence of NaHCO₃ on the other hand decreased sonoluminescence appreciably; organic liquids have similar effects on sonoluminescence in water. Liquids, such as CS₂, B₁₂ and CH₃I enhance the sonoluminescence intensity of water by an order of magnitude. We note that most liquids that do enhance the sonoluminescence of water do not sonoluminesce to any appreciable degree in their pure state. Whereas ethylene glycol and glycerine which luminesce brightly by themselves do not enhance the sonoluminescent intensity of water.

There have been various attempts to correlate the sonoluminescent intensity with liquid properties. Chambers¹⁴ related the intensity to a product of dipole moment of the liquid molecules and the viscosity. More recently, Jarman¹⁵ reported the luminescence intensity to be directly proportional to the square of the surface tension and inversely proportional to the vapor pressure. While discussing some of the other parameters affecting cavitation, we shall introduce an extensive table (Table 2) showing how the various physical properties of the dissolved gas affect the cavitation induced phenomena of sonoluminescence and chemical reaction.

B. Pretreatment of the liquid

It is believed the size of a typical cavitation nucleus depends on the previous history of the liquid. For

example, Flynn¹⁶ states that in fresh tap water that has been allowed to stand open to the atmosphere for a few seconds a typical nucleus radius is 5×10^{-3} cm. In water that has been standing for several hours, the average nucleus has a radius of 5×10^{-4} cm, while water subjected to elevated hydrostatic pressure has an average nucleation radius of 10^{-5} cm (see ref. 16). Even for a liquid free of cavitation nuclei, the bombardment by high energy particles creates minute nuclei of size 10^{-6} to 10^{-7} cm (see ref. 17).

If, prior to cavitation, a liquid is subjected to elevated hydrostatic pressure the average nucleus size is reduced (cavitation threshold increased) because the increased gas solubility in the liquid leads to dissolution of some of the gas present in the nucleus. Harvey¹⁸ reported that after increasing static pressure over water to 1000 atm he could not produce cavitation even after the pressure was released.

C. Nature of the gas

During the rarefaction phase of an acoustic wave a cavitation nuclei grows to some maximum size and then starts to collapse (nearly adiabatically) during the compression phase. The final temperature and pressure for an adiabatic collapse depends on the ratio of specific heats, $\gamma = C_p/C_v$. In fact, a polytropic index n is more appropriate, where $1 < n < \gamma$, in a real situation. Srinivasan¹⁹ studied the spectral distribution of sonoluminescence of water saturated with different gases and found that the spectrum was continuous and that the spectral distribution closely resembled that of a blackbody radiation of 11,000°K for water saturated with monoatomic gases and 8800°K for water saturated with diatomic gases. Triatomic gases like CO₂ suppress both sonoluminescence and sonochemical

Table 2

Effect of physical properties of the dissolved gas on the cavitation induced phenomena of sonoluminescence and chemical reaction

Gas	Molecular weight	Ionization potential (eV)	Specific heat ratio	Solubility in water (ml/100 ml H ₂ O) at 0°C	Thermal conductivity (cal/sec × 10 ⁶ cm ² °C) at 300°K	Specific heat (cal/g mol °C) at 300°K	Amount of H ₂ O ₂ ²¹ formed (10 ⁻⁶ g/ml)	Relative intensity of UV spectra ²¹	Luminous intensity ²² × 10 ⁻¹⁰ (1650A-6500A)
Hydrogen	2	15.6	1.41	2.14	440.0	6.86	—	0	—
Nitrogen	28	15.51	1.40	2.33	61.7	6.80	2.5	45	1.22
Oxygen	32	12.5	1.40	4.89	63.2	6.26	13.5	35	2.44
CO ₂	44	14.4	1.33	171.3	39.2	8.89	0	—	—
Helium	4	24.46	1.65	0.94	357.5	4.97	1	1	1.16
Neon	20.18	21.47	1.64	2.6	114.7	4.97	7	18	3.20
Argon	39.95	15.60	1.65	5.6	42.4	4.97	21.5	54	30
Krypton	83.8	13.93	1.67	11.0	22.6	4.97	24.0	226	50
Xenon	131.3	12.08	1.67	24.1	12.4	4.97	27.5	448	125

reactions. However, different gases with the same specific heat ratio will luminesce with different intensities and also enhance chemical reactions to different extents. This difference may be attributed to departure from adiabatic conditions and to differences in the solubilities of the gases.

(1) *Heat dissipation by conduction:* Departures from adiabatic bubble collapse may be due to heat conduction from the hot bubble contents to the liquid, which essentially acts as a heat sink. If this mechanism is valid, then the thermal diffusivity of the bubble contents should have a pronounced effect on cavitation intensity.

(2) *Effect of heat dissipation on chemical reactions:* Table 2 shows the properties of various gases and their effectiveness in enhancing cavitation phenomena. One observes that the sonochemical yields and the sonoluminescence intensity increase with decreasing thermal conductivity. Fitzgerald *et al.*⁶ studied the effects of the nature of gas on the production of H₂O₂ from water. They systematically varied the

gas composition of an argon-helium mixture from pure argon to pure helium. From Fig. 1, we observe that over most of the composition range the thermal conductivity of the gas mixture is linearly dependent on percent argon as is the yield of H₂O₂. In Fig. 2 the yield of H₂O₂ is plotted as a function of the square root of the thermal conductivity of the gas mixture. One may recall that the unsteady state heat flux from a semi-infinite medium is proportional to the square root of the thermal conductivity of the medium. The linear dependence of the H₂O₂ yield on the square root of the thermal conductivity, as shown in Fig. 2, is sometimes cited as evidence in support of the "hot spot" theory of bubble collapse. However, as we will show later, the H₂O₂ yields also correlated equally well with gas solubility.

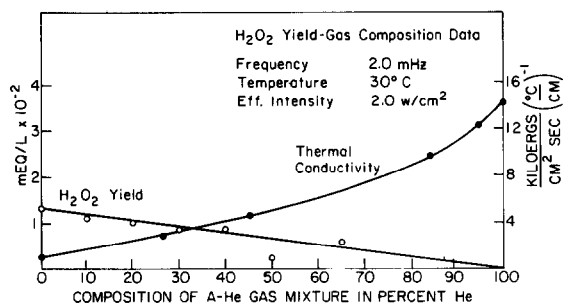


Fig. 1. Effect of thermal conductivity of dissolved gas on sonochemical reactions⁶.

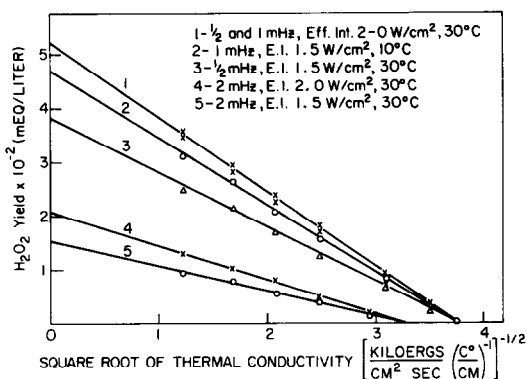


Fig. 2. Dependence of sonochemical reaction yields on thermal conductivity of dissolved gas⁶.

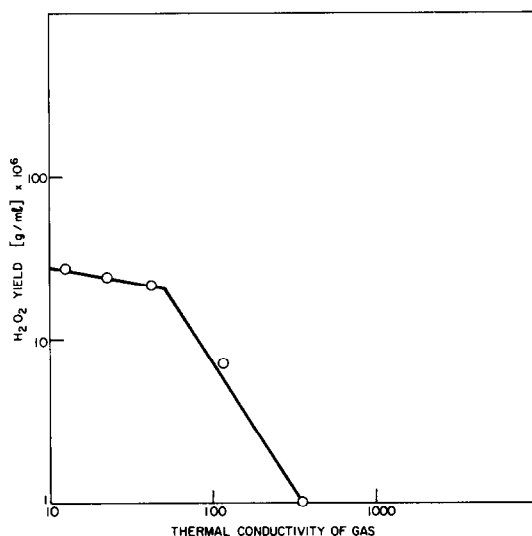


Fig. 3. Dependence of sonochemical reaction yields on thermal conductivity of dissolved gas²¹.

Prudhomme and Guilmart²¹ also studied the effect of the nature of the dissolved gas on the yield of H₂O₂ from water. Using their data on the rare gases, we have constructed a plot of H₂O₂ yields vs. the gas thermal conductivity in Fig. 3. The plot shows an increasing yield of H₂O₂ with decreasing thermal conductivity of the gas up to a point beyond which the yield remains essentially the same on further reduction of the thermal conductivity of the gas. This suggests that there is a region in which the bubble collapse is adiabatic and one in which it is heat transfer controlled. A third region is, of course, one in which the collapse is isothermal.

(3) *Effect of heat dissipation on sonoluminescence:* If heat is conducted away from collapsing bubbles the temperatures reached in the final stages of collapse will be reduced. This reduced temperature is reflected in the differing sonoluminescent intensity for groups of gases with identical specific heat ratios. The work of Pruhomme and Guilmart²¹ and Young²² is summarized in Table 2 along with pertinent physical property

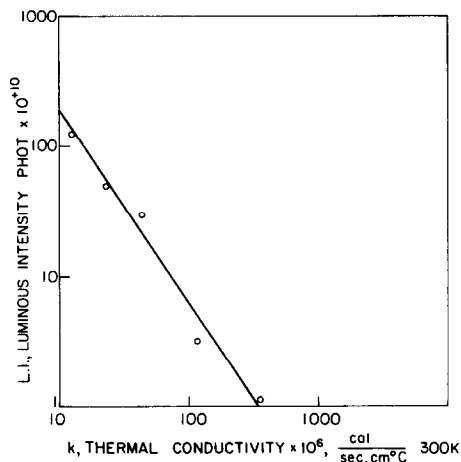


Fig. 4. Effect of thermal conductivity of gas on sonoluminescence: Reinterpreted and replotted data of ref. (22); L.I. (Phots x 10¹⁰) = 5850 [k (cal/sec cm °C)]^{-1.50}.

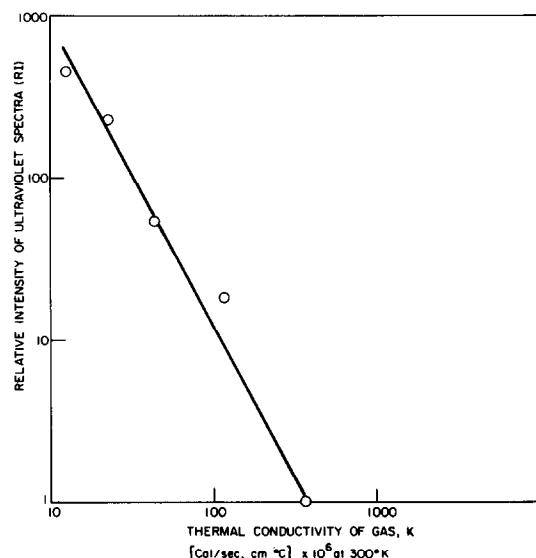
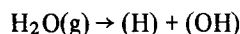


Fig. 5. Effect of thermal conductivity of gas on sonoluminescence²¹; L.I = 3.3 x 10⁶ [k]^{-1.8}.

data we have gathered for each of the gases used in their studies. We have used the data obtained by Young²² to construct a plot of luminous intensity *versus* the thermal conductivity to obtain Fig. 4, and the data obtained by Prudhomme and Guilmart²¹ to obtain Fig. 5. Again we especially note the trend of increasing sonoluminescence with increasing gas solubility. (See Table 2 and Figs. 6 and 7.)

(4) *Heat dissipation due to chemical reaction:* One source of heat dissipation often overlooked in previous studies is that absorbed by the heat of reaction from the dissociating water vapor molecules in the gas bubble. The dissociation



is highly endothermic, with a heat of reaction, $\Delta H_R = 54.933 \text{ kcal/g mol}$.

We shall now undertake some *very approximate* calculations to ascertain the effect of endothermic reactions occurring during collapse on the temperature of the gas bubble. The "energy accumulation" Q_C due to adiabatic collapse in the absence of chemical reaction can be approximated by

$$Q_C = \frac{NR}{\gamma - 1} [T_2 - T_1] \tag{1}$$

where N is the number of g moles of gas in the cavitation bubble, R is the ideal gas constant, γ is the specific heat ratio, and T_1 and T_2 are the initial and final temperatures, respectively. For a pressure amplitude of 3 atm, an initial bubble radius of 10⁻⁴ cm and an initial pressure in the bubble of 0.01 atm, there will be 1.71 x 10⁻¹⁸ g mole of gas in the bubble. If 50% of the contents of the bubble are assumed to be water vapor, this corresponds to 8.55 x 10⁻¹⁹ g mole H₂O in the bubble.

On compression, the amount of heat generated, calculated from eqn. (1) assuming $T_1 = 300^\circ\text{K}$, $T_2 = 10,000^\circ\text{K}$ and $\gamma = 1.67$ is, $Q_C = 4.902 \times 10^{-14} \text{ cal}$.

If Z is the number of moles of H₂O dissociating we have, the "heat absorbed by the reaction", is $Q_R = 54.933 \times 10^3 Z \text{ cal}$. The ratio of Q_R to Q_C is

$$\frac{Q_R}{Q_C} = \frac{\text{heat absorbed by endothermic reaction}}{\text{heat generated due to compression}} = 1.121 \times 10^{18} Z \tag{2}$$

Equation (2) is evaluated in Table 3 for various fractions of water vapor in the bubble dissociating.

TABLE 3

Evaluated values of Q_R/Q_C for 8.55×10^{-19} mole of H_2O initially in the bubble

Fraction of H_2O dissociating	Number of moles of H_2O dissociating, Z	$\frac{Q_R}{Q_C} = \frac{\text{Heat of reaction}}{\text{Heat of compression}}$
0.01	8.55×10^{-21}	0.00958
0.1	8.55×10^{-20}	0.0958
1.0	8.55×10^{-19}	0.958

Hence, we see that if H_2O in the bubble is dissociating into (H) and (OH) radicals a portion of the heat of compression is absorbed by this dissociation thus lowering the final temperature in the bubble. This source of heat dissipation has not been taken into account in previous studies. A possible explanation of the inhibitive action of dissolved CO_2 on sonoluminescence and chemical reactions may be the thermal dissociation of CO_2 to CO and O_2 in the cavitation bubble resulting in a lower bubble temperature.

(5) *Effect of gas solubility*: We believe that the effect of this variable on cavitation phenomena has been *greatly* under-estimated in past work. In studying the effect of gas solubility on cavitation erosion, Bebachuk and Rozenburg²³ found that erosion decreased monotonically with increased gas solubility. Fitzgerald⁶ and Prudhomme²⁴ observed the effect of various dissolved gases in promoting the formation of H_2O_2

from water. As mentioned previously, Fitzgerald varied the composition of an argon-helium mixture over the range of 0 to 100% argon and found that the H_2O_2 yield decrease linearly with the square root of the thermal conductivity of the gas mixture. In Fig. 6 we have *replotted* Fitzgerald's data as a function of amount of dissolved gas over the same gas composition range. In calculating the quantity of dissolved gas we used Henry's law and assumed a saturated solution at a total pressure of 1 atm. It can be seen that the H_2O_2 yield is *also* linearly related to the quantity of dissolved gas. We believe this points to the statistical relationship between cavitation and amount of dissolved gas.

Prudhomme and Guilmar²¹ and Young²² studied the sonoluminescent intensity of water in the presence of various dissolved gases. To demonstrate the effect of solubility we have *replotted* their data in Fig. 7. Again one can see the trend towards increasing sono-

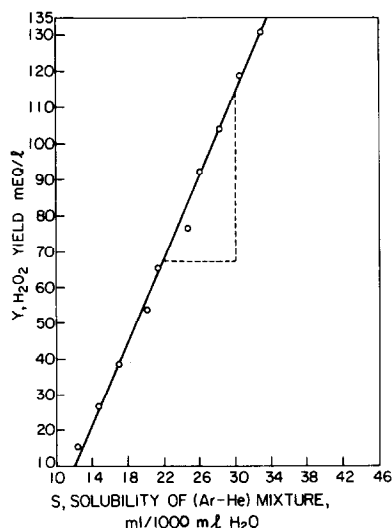


Fig. 6. Effect of gas solubility on sonochemical reaction yields: Reinterpreted and replotted data of ref. (6); $y[\text{mEq/l}] = 5.88 S[\text{ml gas}/1000 \text{ ml } H_2O] - 61.9$.

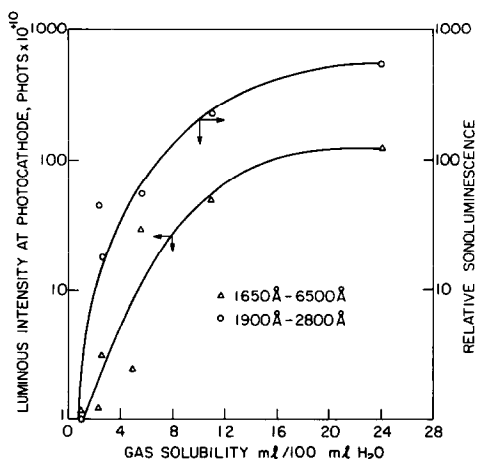


Fig. 7. Effect of gas solubility on sonoluminescence: Reinterpreted and replotted data of refs. (21) and (22).

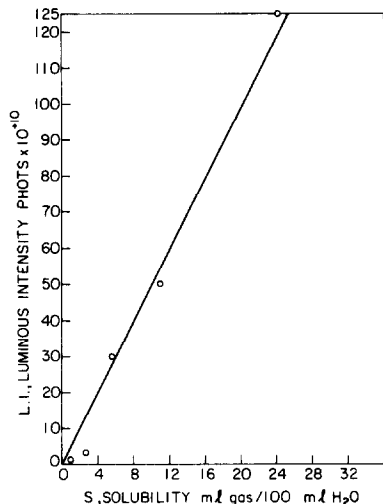


Fig. 8. Effect of gas solubility on sonoluminescence intensity for gases with the same specific heat ratios ($\gamma = 1.67$): Reinterpreted and replotted data of ref. (22); L.I. [PHOTS x 10^{10}] = $2 S$ [ml gas/100 ml H₂O].

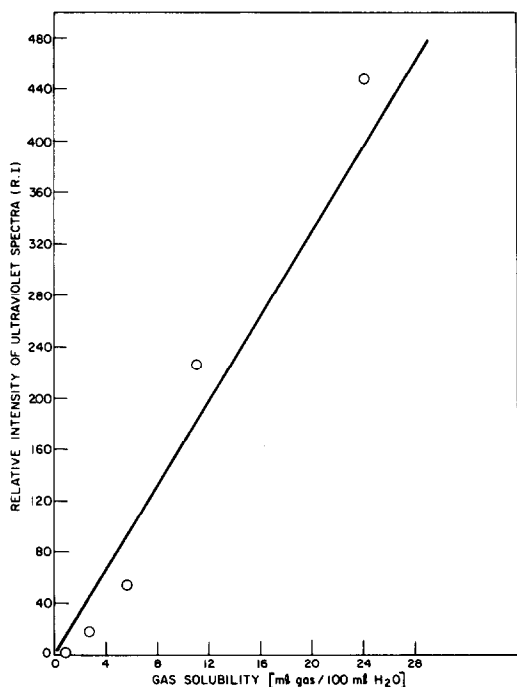


Fig. 9. Effect of gas solubility on intensity of ultraviolet spectra for gases with the same specific heat ratios ($\gamma = 1.67$): Reinterpreted and replotted data of ref. (21); R.I. = 1.67 (solubility).

luminescence with increasing amounts of dissolved gas. In Figs. 8 and 9 we have *replotted* the dependence of sonoluminescent intensity on gas solubility for gases with identical specific heat ratios. Again one observes the linear dependence of sonoluminescence intensity on gas solubility. It may be recalled that in Fig. 6 a similar linear dependence of H₂O₂ yield on solubility was obtained.

In a recent article, Ceschia *et al.*²⁵ proposed a model which assumes that the concentration of cavitation nuclei is directly proportional to gas solubility. In their experiments they observed a decrease in cavitation threshold for incipient sonoluminescence with increasing gas solubility.

D. Effect of hydrostatic pressure

On increasing static pressure over a liquid some of the gas from a cavitation nucleus dissolves in the surrounding liquid thus diminishing its radius. As shown by Sirotiyuk²⁶, the nucleation strength of the liquid rises as the bubble nucleus radius decreases. An increase in static pressure also reduces the *gas content* of a bubble. Gas content is defined as the ratio of gas pressure in the bubble at maximum dilation to the static pressure over the system. In a numerical study of the bubble collapse equation, Akulichev²⁷ reports that decreasing the gas content by a factor of 10^{-2} increases the maximum pressure reached at the final stage of collapse by a factor of 10^4 . It is clear that if the collapse is approximately adiabatic, the final temperature will also increase with decreasing gas content. To summarize the effects of elevated static pressure we note that increasing the static pressure: (1) Decreases the gas content of a bubble, (2) Increases maximum pressure during the final stages of collapse, (3) Increases temperature reached during the final stages of collapse, (4) Increases erosion, which depends on shock wave intensity, (5) May or may not increase chemical reaction yields. The chemical reaction rate will increase with increased final temperature and pressure associated with higher static pressures (lower gas content). However, a lower gas content also means a lower concentration of gas molecules in a bubble thus lowering the reaction rate and reaction product yield. Depending on which of these two effects is greater, elevated static pressure may or may not enhance sonochemical reaction yields.

Agranat *et al.*²⁸ showed that increasing static pressure over a liquid can lead to an increase in the mechanical impedance of a cavitating liquid. This improved mechanical impedance results in increased acoustic power being transferred to the liquid without

TABLE 4

Effect of elevated static pressure on cavitation processes

<i>Author</i>	<i>System studied</i>	<i>Nature of effect</i>
Weissler ³⁰	Yield of H ₂ O ₂ Sonoluminescence	Shows a maximum yield at 2 atm Shows a maximum intensity at 2 atm
Finch ³¹	Sonoluminescence of H ₂ O	Luminescence increases with pressure in the range of 0–10 psi; then decreases with further pressure increases
Siryotuk ³²	Cavitation, erosion Sonoluminescence	Erosion increases with pressure by a factor of 10 ² to 10 ³ until a pressure of 45 atm then starts decreasing with a further increase in pressure Luminescence intensity decreases with pressure up to 30 atm then increases with increasing pressure
El'Piner ³³	Oxidation of KI in aqueous solution in presence of O ₂	Yield decreases monotonically from 1 to 40 atm pressure
Bronskaya <i>et al.</i> ³⁴	Formation of HCOOH from α ketoglutaric acid Irradiation of biological cells	Yield decreases with increasing pressure from 1 to 4 atm then starts to increase Mortality of cells rises abruptly when pressure is increased above 4 atm
Fogler ³⁵	Decomposition of CCl ₄ in presence of argon	Yield of Cl ₂ increases up to a pressure of 1.8 atm (higher pressures not investigated owing to equipment limitations)
Bogachev <i>et al.</i> ²⁰	Cavitation erosion in liquid oxygen	The cavitation erosion vs. static pressure curve shows a maximum at a pressure which depends on applied acoustic frequency

any increase in the electrical consumption by the transducer. The optimum static to acoustic power ratio for maximum acoustic power was 0.4.

Table 4 summarizes the effect of elevated hydrostatic pressure on cavitation phenomena.

E. Effect of ambient liquid temperature

The ambient liquid temperature determines the gas solubility and liquid vapor pressure. On decreasing liquid temperature, the amount of gas dissolved increases and the vapor pressure of the liquid decreases. In addition to changing the radius of nuclei, a change in liquid temperature will affect the gas content and the relative ratio of gas to vapor in a bubble.

(1) *Effect of liquid temperature on sonochemical reactions:* Most authors have reported a monotonic decrease in sonochemical yields with increasing liquid temperature [Ibishi and Brown³⁵, Sokol'skaya and El'Piner³²]. In Sokol'skaya and El'Piner's work on the

synthesis of NH₃ from N₂ and H₂ dissolved in water, the yield of NH₃ increased by a factor of 3 when the liquid temperature was decreased from 60°C to 10°C. We have calculated the solubilities of nitrogen and hydrogen using Henry's law for temperatures from 10° to 60°C in Table 5.

As a first approximation one may assume that the chemical reaction rates are proportional to the product of the solubilities of nitrogen and hydrogen. In Fig. 10 the ratio of solubility products and the ratio of reaction yields at a given temperature to the respective quantities at 60°C are compared. The close agreement indicates that the increased solubilities are probably responsible for the increased reaction yields.

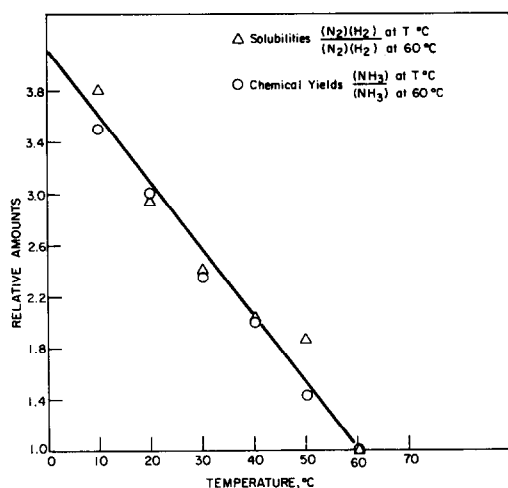
One additional factor should also be considered from Sokol'skaya and El'Piner's³² work. After 1 hour of irradiation of N₂-H₂ saturated solution at 750 kHz, 10 watts/cm² and 60°C liquid temperature, we calculated that 10.3% of the originally dissolved hydrogen was consumed. Under similar conditions at 10°C, 52.0% of the originally dissolved hydrogen was consumed.

TABLE 5

Comparison of calculated solubility values of N_2 and H_2 with reaction yields

Temperature ($^{\circ}C$)	Solubility of gases (ml gas/100 ml H_2O)		Ratio of products of solubilities,	Ratio of NH_3 yields,
	N_2	H_2	$\frac{[N_2 \cdot H_2] T}{[N_2 \cdot H_2] 60^{\circ}C}$	$\frac{[NH_3 \text{ yield}] T}{[NH_3 \text{ yield}] 60^{\circ}C}$
10	18.6	19.6	3.80	3.50
20	15.5	18.2	2.94	3.0
30	13.5	17.1	2.41	2.36
40	11.9	16.6	2.06	2.0
50	11.0	16.3	1.87	1.43
60*	8	12	1.0	1.0

* Values reported by Sokol'skaya and El'Piner.

Fig. 10. Effect of gas solubility on sonochemical reaction yields³².

At some point, therefore, the rate of dissolution of H_2 in water from the gas phase may become a limiting factor in the sonochemical synthesis of NH_3 .

(2) *Effect of liquid temperature on sonoluminescence:* Gunther *et al.*³⁶ and Siryotuk³⁷ have shown that sonoluminescence, which follows some of the same trends as sonochemical reactions, decreases monotonically with increasing liquid temperature. Recently Samek and Tarba³⁸ studied the sonoluminescence of distilled water at a frequency of 43.41 kHz in the temperature range of $5^{\circ}C$ to $45^{\circ}C$ and found the intensity of sonoluminescence decreased when the ambient liquid temperature was increased.

(3) *Effect of liquid temperature on cavitation erosion:* There is some disagreement in the literature

on the effect of ambient liquid temperature on cavitation erosion. Ibishi and Brown³⁵ and Bebhuk³⁹ report a maximum in the cavitation erosion at a temperature of approximately $50^{\circ}C$. Siryotuk²⁶ on the other hand reports a monotonic decrease in cavitation erosion when liquid temperature is increased.

The apparent discrepancy can be resolved by noting that as the liquid temperature is increased the vapor pressure in the bubble nuclei increases and also some dissolved gas comes out of solution into the bubble. These factors increase the average radius of the cavitation nuclei and increase the number of active bubbles, (*i.e.* cavitation zone). However, the increased air content at higher liquid temperatures should produce lower cavitation intensity. If the test specimen is smaller than the cavitation zone the increase in the size of the zone with temperature is of no consequence. For such a specimen the erosion rate will decrease due to the lower intensity of cavitation. However, for a test specimen larger than the cavitation zone the enlargement of the zone means a large area of the specimen is exposed to attack but at a decreased intensity. These competing phenomena may explain the maximum in the temperature-cavitation erosion curve obtained by Ibishi and Brown³⁵ and Bebhuk³⁹ but not by Siryotuk²⁶.

F. Effect of acoustic intensity (Pressure amplitude) Corresponding to a given distribution of nuclei sizes there is a minimum acoustic pressure amplitude, called the threshold pressure amplitude, necessary to produce cavitation. As the acoustic pressure amplitude is increased, smaller bubbles become unstable and start contributing to cavitation activity. The maximum bubble radius also increases with acoustic pressure amplitude and is essentially independent of initial bubble size. Hence, as the acoustic intensity is increased,

both the number of bubbles and their maximum size increases resulting in increased cavitation activity. This increase is not indefinite, however, because as the maximum radius of a bubble increases so does the Rayleigh collapse time. If the collapse time becomes greater than the half period of the wave, the cavitation bubble will not have time to collapse before the sound field reverses itself and the rarefaction phase of wave begins acting on the collapsing bubble. Hence, the number of collapsing bubbles, and therefore cavitation intensity, will decrease. A maximum acoustic intensity is feasible provided the Rayleigh collapse time is equal to or less than one half the period of the acoustic wave.

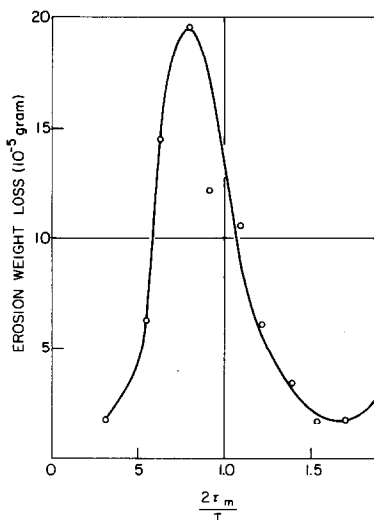


Fig. 11. Dependence of sonoluminescence on acoustic parameters⁴⁰.

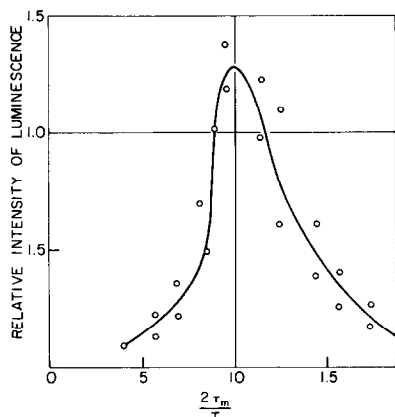


Fig. 12. Dependence of cavitation erosion on acoustic parameters.

The existence for an optimum pressure amplitude for a given frequency has been demonstrated for some cavitation related phenomena [e.g., Sonoluminescence⁴⁰, Cavitation Erosion⁴¹]. Figures 11 and 12 illustrate the existence of an optimum pressure amplitude for sonoluminescence and cavitation erosion.

The effect of pressure amplitude on sonochemical reactions has not exhibited a maximum. Thus, yields increase with increasing amplitude. This may, however, be due to the fact that high intensity ultrasonic horns have not been used so far in studying sonochemical reactions.

G. Effect of acoustic frequency

Esche⁴² has shown that the cavitation threshold is strongly frequency dependent. For a given acoustic field only those bubbles with a resonance frequency greater than the acoustic frequency will cavitate. Consequently, as the acoustic frequency is increased, the size of a cavitating bubble decreases resulting in an increase in the cavitation threshold. An increase in frequency also means shorter acoustic periods hence lower maximum bubble size and thus less cavitation intensity. Sonochemical reactions have been found to be relatively insensitive to ultrasonic frequency probably because most commercial transducers do not have large enough pressure amplitudes. Acoustic frequency might become a factor in focusing transducers or horns.

H. Applications

Some of the major industrial operations which have been enhanced by the application of acoustic wave include defoaming, drying emulsification and extraction.

3. DEFOAMING

The necessity of breaking foams arises often in many industrial operations as well as in sewage treatment plants⁴³⁻⁴⁸. The ultrasonic techniques used in breaking foams are mechanical and have the advantage that one does not have to add a chemical contaminant to break the foam. Most liquids with viscosities up to 500 cP can be defoamed. Although the exact mechanism of acoustic foam disintegration is not entirely understood, the following acoustic effects are believed to be most important in foam breakage: (a) the instability of varicose waves in the foam film induced by acoustic waves (preliminary studies on single liquid films in our laboratory have clearly demonstrated the presence of this type of wave); (b) cavitation; (c) atomization was observed to occur from the film surface; (d) the

acoustically induced convective streaming currents we observed may produce high shear stresses which result in foam rupture. One investigator reports⁴⁹ that there is evidence that there is a critical sound pressure level at which a column of foam would collapse catastrophically while another⁵⁰ indicated that there was an optimum frequency at which the defoaming rate was at a maximum. In this latter study, there was no mention as to whether or not the sonic power was constant. In studies in our laboratory we initially observed what we thought was a very similar frequency dependence; however, on measuring the acoustic intensity at the various frequencies, it was found that the maximum intensity of the loudspeaker system corresponded to the frequency that gave the maximum defoaming rate. Consequently, the existence of an optimum frequency is doubtful and the effect of frequency on the rate of defoaming is uncertain at this time.

A number of other authors have reported⁵¹⁻⁵⁹ various applications of acoustic defoaming to such processes as fermentation, pumping of jet fuel oil and others. In summary, acoustic defoaming is a particularly viable alternative when the addition of a chemical defoaming agent will contaminate the liquid to be defoamed.

4. EMULSIFICATION

Acoustic emulsification is believed to result from mechanisms similar to those thought responsible for producing acoustic defoaming⁶⁰. An emulsion will be rapidly formed when an acoustic wave of sufficient intensity is applied to two immiscible liquids. In our laboratory we have observed the mean acoustic emulsion particle size with the aid of a scanning electron microscope to range from 0.18 to 0.37 microns. In addition to acoustic emulsification producing these submicron particles, the resulting particle size distribution is extremely narrow.

Ever since acoustic emulsification of oils and of mercury in water was first noted by Wood and Loomis⁶¹ in 1927, it has become increasingly popular in dairy, petroleum, pharmaceutical, and similar industries and has greater potentiality in a number of technological processes for supplanting existing methods⁶²⁻⁶⁷. An excellent discussion on the fundamental principles of emulsion formation has been given recently by Gopal⁶⁸. Acoustically induced interfacial instability at the liquid-liquid interface is believed responsible for producing the emulsion at high acoustic frequencies

while cavitation is believed responsible at lower frequencies. A discussion of the various mechanisms involved in acoustic emulsification is given by Fogler⁶⁰. A number of authors⁶⁹⁻⁹³ have also reported on various aspects of acoustic emulsification.

5. ACOUSTICALLY ENHANCED MASS TRANSFER

A. Extraction

One of the mass transfer operations which appears to be the most greatly enhanced by the application of ultrasonic waves is solid-liquid extraction. The pioneering work in this area was done by Thompson, who applied 400 kHz ultrasonic waves to peanut oil and observed increased rates of extraction using *n*-hexane as a solvent⁹⁴.

A thorough review of the use of ultrasonics in the extraction of pharmaceuticals is given by Skauen⁹⁵. While cavitation induced cell disruption to release the entrapped oils or solutes is believed to be the primary mechanism for bringing about these increases, emulsification, and microstreaming are also contributing factors in the acoustically induced enhancement of solid-liquid extraction. Ultrasonic waves have been applied to the various extraction processes and enormous increases in the rate of extraction have been reported by a number of investigators⁹⁶⁻¹⁰¹.

B. Drying

Ultrasonic drying finds one of its greatest uses in drying of heat-sensitive materials such as those found in the pharmaceutical and food industries. Soloff¹⁰⁵ found a two- to five-fold increase in drying rates with acoustic waves. Using ultrasonics in drying has an advantage over drying with high velocity steady gas currents which might blow away or damage the product. Enhancement in drying rates has been recently reported by Wilson¹⁰⁶ and by Purdy¹⁰⁷. Other investigators have observed increased rates using acoustic waves in a variety of systems¹⁰⁸⁻¹¹³. While the exact mechanism believed responsible for bringing about these increases is uncertain, one of the leading theories is that acoustic vibrations cause the liquid contained in the internal pores of the porous media to rise to the surface very rapidly⁶⁰. Other factors responsible for accelerating the acoustic drying phenomena include microstreaming, atomization of the liquid in the pores and modification of the mass transfer boundary layer surrounding the porous sample.

6. MISCELLANEOUS

Rod¹¹⁴, Walker¹¹⁵ and Steinberg¹¹⁶ have published reviews on the use of ultrasonics in production operations. Ultrasonic waves have been found to enhance electroplating operations in a number of instances¹¹⁷⁻¹²². Other processes and equipment used in sonochemical processing include a sonic dispersing device¹²³, a sonic distillation process¹²⁴, an apparatus for ultrasonically degassing metallic melts¹²⁵, polymer processing¹²⁶, and a device which disperses and produces crystals of uniform sizes¹²⁷⁻¹²⁹. The use of acoustic devices in instrumentation is receiving increasing attention in the areas of ultrasonic flow meters¹³⁰, ultrasonic thermometers¹³¹ and in holography¹³².

The agglomeration of aerosol particles by ultrasonic devices has been achieved¹³³⁻¹³⁶. In addition to the development of demisting devices, ultrasonics have been used in the sensing and counting of minute aerosol particles¹³⁷. These minute aerosol particles can be produced by ultrasonically irradiating liquids. This ultrasonic atomization is particularly efficient if the liquid height is maintained in a resonant wave condition¹³⁸. The mean particle size of the atomized particles may be varied by varying the frequency of the ultrasonic wave¹³⁹. These two phenomena just discussed suggest the synthesis of a self-contained ultrasonic unit; that is, one could ultrasonically produce aerosol particles by ultrasonic atomization and then incorporate the ultrasonic demister to eliminate them.

7. CONCLUSION

A number of unusual phenomena are observed when acoustic waves are passed through liquids and gases. In studying the effect of various parameters on cavitation processes, it appears that inadequate emphasis has been placed on the role of gas solubility. We have reinterpreted some of the existing data on sonoluminescence and sonochemical reactions and found a linear dependence of these phenomena on the solubility of dissolved gas. This suggests a statistical relationship between amount of dissolved gas and cavitation events. We have also shown that if an endothermic reaction such as the dissociation of water vapor occurs in a bubble, the bubble collapse temperature can be drastically affected by the degree of dissociation. In addition, the various industrial processes in which the application of sonic and ultra-

sonic energy offers an attractive alternative to existing procedures have been outlined.

The phenomena of cavitation, acoustic streaming, and surface instabilities have produced increased rates of heat and mass transfer, chemical reactions, defoaming, and emulsification in a wide variety of chemical and physical processing systems. With the advent of newer, less expensive, and more powerful ultrasonic generators, it is anticipated that ultrasonics will play an even greater role in chemical processing.

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