THE APPLICATION OF SONIC AND ULTRASONIC WAVES IN COLLOID CHEMISTRY

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Received September 28, 1943

I

Low-frequency audible as well as high-frequency inaudible sound waves ("ultrasonics") of great intensity are able to produce a great diversity of phenomena pertaining to the realm of colloid chemistry (86). They may bring about various dispersion effects, such as the mutual emulsification of two bulk liquid phases, the disintegration of certain solids, peptization, the liquefaction of gels, the depolymerization of high-molecular substances, the formation of fogs, etc. On the other hand, they may also cause accumulation, aggregation, and coagulation; with anisometric particles, orientation in liquid as well as in gaseous systems may result. In addition, sound waves degas liquids and always heat the irradiated systems; they further favor the formation of new phases in some instances, e.g., they start crystallization from many supersaturated solutions and affect the crystalline structure of metals and alloys when applied to the melts during the period of cooling and crystallization.

There are no fundamental physical differences between sound waves of low, medium, and high frequencies; however, great differences exist in the case of their production and transmission. Originally ultrasonics of several hundred thousand cycles per second were used exclusively for colloid work; later, frequencies down into the audible range have come into more general use. At very high frequencies the energy losses become excessive.

Four main groups of sound generators have been used for colloid work: (*a*) piezoelectric; (*b*) magnetostrictive; (*c*) electromagnetic sound generators; and (*d*) the gas current vibration generator, a device useful only in gaseous systems.

The *piezoeletric sound generator* transforms high-frequency electric oscillations into mechanical oscillations by making use of the piezoelectric effect. For colloid work the frequency range from 100,000 to 1,000,000 cycles a second is used.

If an alternating electrical field is applied to a piezoelectric crystal, e.g., a quartz crystal plate, the crystal contracts and expands periodically—it vibrates. The frequency of these vibrations is that of the applied electrical field. At a given field strength the vibrations become much stronger if the quartz oscillator vibrates in resonance; then electrical energy can be transformed efficiently into mechanical oscillations.

In gases the energy transmission from the solid oscillator to the surrounding medium is very poor. If, however, a quartz crystal vibrates in a liquid, then the energy transfer is good and the useful energy output may become rather high.

For most work on colloids one immerses the quartz oscillator with a suitable electrode system in a bath of oil which transmits the vibrations easily to any other system dipped into it (2, 30, 32, 35, 43, 86). The electrical oscillations which operate the crystal are generated by an electronic oscillator with an energy output of several hundred watts. It is coupled to the electrode system by means of a Tesla coil. Figure 1 shows the general scheme of the piezoelectric generators; figure 2 is a photograph of the apparatus used by the author; figure 3 shows a quartz oscillator and an electrode system in an oil bath, as used, e.g., for emulsification.

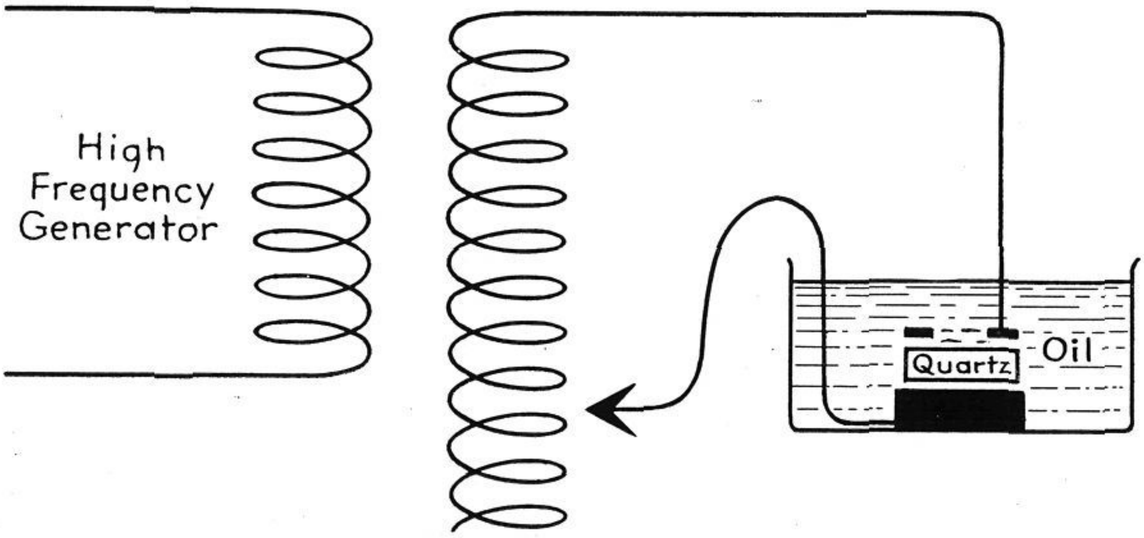

FIG. 1. Piezoelectric sound generator

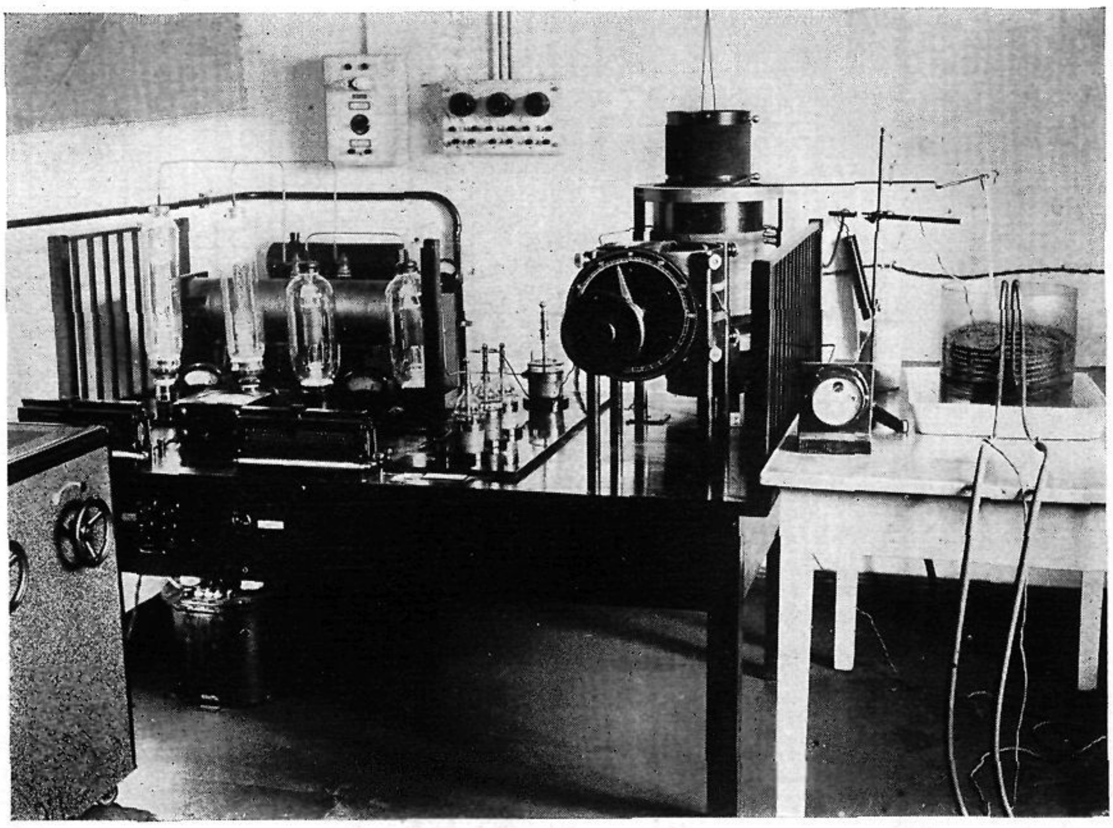

FIG. 2. Laboratory model of piezoelectric sound generator (from K. Sollner)

The *magnetostriction generator* transforms alternating electric currents into sound vibrations, making use of the magnetostriction effect (61).

A rod or tube of ferromagnetic material brought into a magnetic field parallel to its axis decreases or increases in length, depending upon the nature of the material, its previous treatment, the applied field strength, and other factors. This effect is known as "magnetostriction."

In an alternating magnetic field the length of the rod changes periodically by magnetization. Resonance between the natural elastic period of the rod and the frequency of oscillations caused by the magnetic field increases the efficiency of the energy transformation greatly.

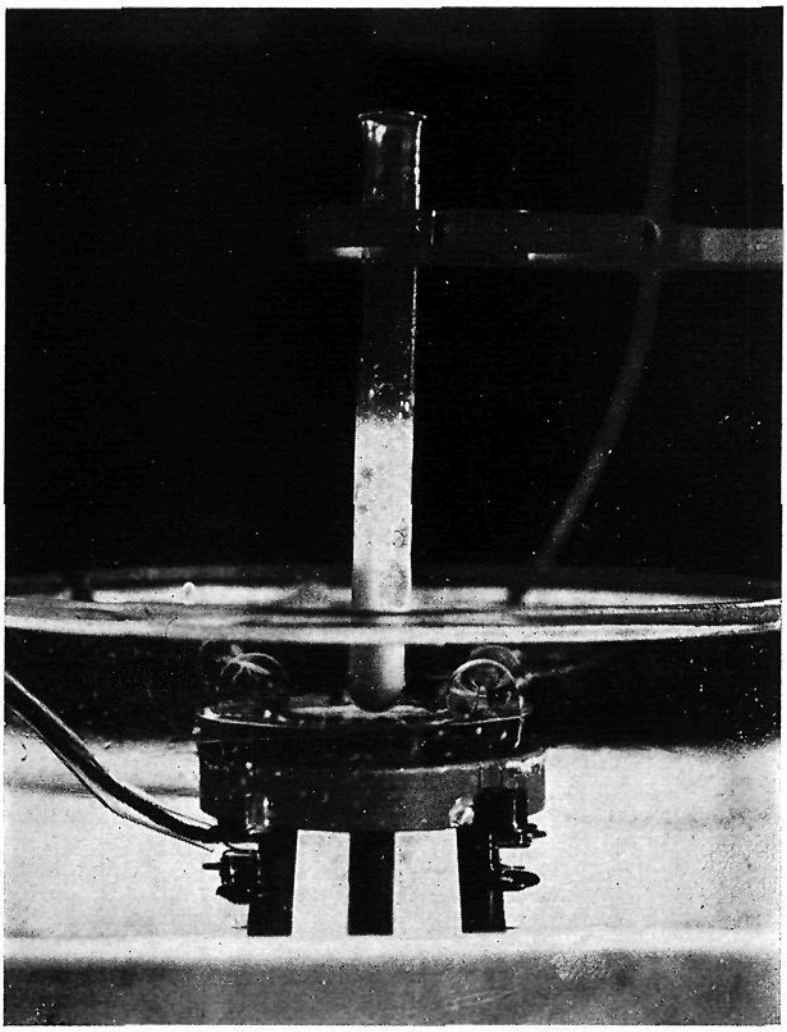

FIG. 3. Quartz oscillator and electrode system of a piezoelectric sound generator in an oil bath as used for emulsification (from K. Sollner).

The alternating magnetic field used in the magnetostriction sound generators is produced by an alternating electric current (14, 15, 16, 26). Figure 4 shows the construction of a laboratory model described by Chambers and Flosdorf (14).

Such generators are used in liquid as well as in gaseous systems; in the latter case a large piston-like end-plate affixed to the vibrating tube facilitates the transmission of energy into the gaseous phase. The range of useful application is from several thousand up to 50,000 cycles a second. The corresponding relatively great length of the sound waves is one of the main disadvantages of these generators for work in liquid systems. Their advantages are their relatively simple and cheap construction and the fact that the oscillator itself—usually a vibrating nickel tube—may in most cases be brought in direct contact with the substances to be treated without the interposition of another medium. It seems likely that magnetostriction generators will at least partially displace piezoelectric oscillators for colloid work.

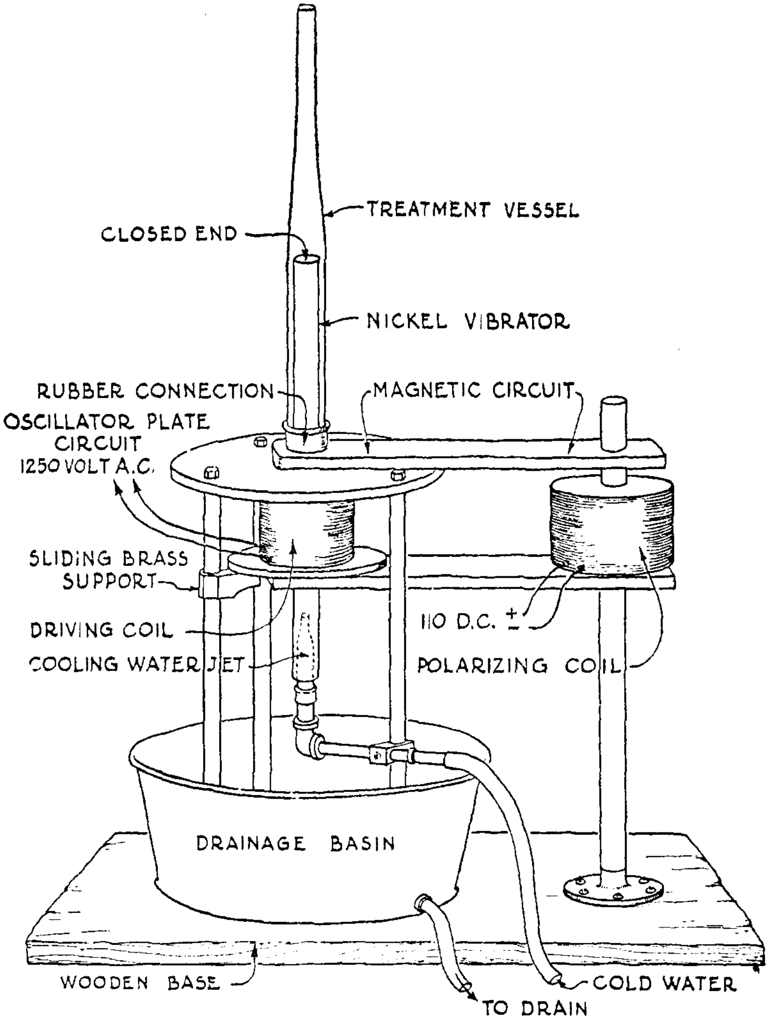

FIG. 4. Magnetostriction sound generator (from L. A. Chambers and E. W. Flosdorf); reproduced by permission.

The *electromagnetic sound generators* have so far been used in only a few cases. Their frequency is entirely in the lower audible range.

Chambers (10) describes two types of oscillators, one of conventional electromagnetic design, and one of the Fessenden type. The electromagnetic oscillators are similar to those used in submarine communication and echo depth sounding; they consist essentially of a heavy steel membrane actuated by alternation in an electromagnetic circuit. The oscillators of the Fessenden type have the vibrating membrane fixed to a copper tube, the whole being polarized by an alternating inciting current. The movement of the diaphragm depends on reversal of eddy currents in the copper tube induced by current oscillations in an activating coil. Clair (16) developed a generator for the study of the coagulation of smoke; it is claimed to be very efficient. All these devices are operated at their natural resonance frequency.

Since only a few investigators have used electromagnetic sound generators, it is difficult at present to appraise their merits justly. They are very promising in the treatment of gaseous systems. If it should be found possible to operate electromagnetic sound generators really efficiently in liquid systems, it seems likely that this method could find wide industrial application.

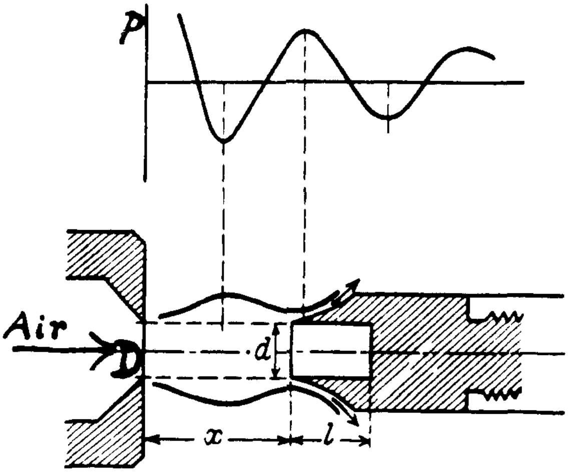

FIG. 5. Gas-current sound generator

Gas-current vibration generators are designed for attaining great energies of vibration in gases (Hartmann (33)). If a current of air is allowed to issue from a nozzle at a speed greater than sound velocity, a periodic structure is formed in the air stream. The pressure, P, varies periodically at different distances from the mouth of the nozzle, D, as indicated in the upper half of figure 5. This makes possible the production of sound waves when a hollow body, serving as an oscillator, is brought into these regions of instability (figure 5, lower half). The frequencies of the sound waves are determined by the dimensions l and d of the hollow oscillator, and its distance x from the nozzle D. Thus one is able to produce oscillations ranging from infra-acoustic up into high ultrasonic frequencies. The gas-current vibration generator may find an important application in the coagulation of industrial smokes and fogs.

II

Emulsification occurs if a test tube containing water and mercury, or water and an immiscible organic liquid, is dipped into the vibrating oil of a piezoelectric sound generator, or if the same two-phase systems come in contact with the vibrating nickel rod of a magnetostrictive sound generator. Grey clouds of very fine mercury droplets are thrown into the water from the water–mercury interface; in oil–water systems white clouds of dispersed water and organic liquid, respectively, are produced where the two liquids meet and soon more or less concentrated emulsions are formed (compare figure 3). In small-scale experiments 6 g. of mercury per liter and 60 g. per liter of benzene or similar substances may be dispersed in 1 or 2 min.; in the absence of any protecting or stabilizing agent these concentrations do not increase on further irradiation. In the presence of suitable emulsifiers very high concentrations can be obtained.

The mechanism of dispersion of liquid and molten metals according to Richards (65; see also 78) is as follows: When the vessel containing the metal and the water is irradiated, violent transverse vibrations are set up in the walls of the vessel and small quantities of water are pumped into the liquid metal; the water droplets rise through it and reach the interface metal–water covered with a thin film of metal. This film breaks and a cloud of minute metal droplets is thrown into the water. This obviously occurs also between the water droplets in the interior of the liquid metal. A low-melting alloy cooled during irradiation, therefore, as shown by Sollner (76), is sponge-like (figure 6). This mechanism of the formation of mercury sols by sound waves is basically the same as by normal mechanical dispersion (Nordlund (55)).

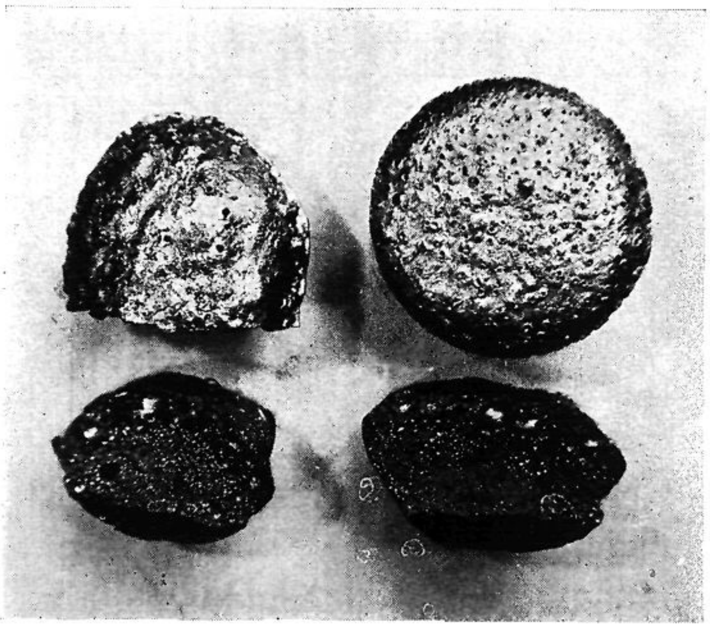

FIG. 6. Emulsification of a metal by ultrasonics: a low-melting alloy solidified during irradiation. About twice actual size. (From K. Sollner)

Harvey (35) showed that in non-metallic systems emulsification occurs neither *in vacuo* nor when sufficiently high outside pressure is applied. This rule applied even in the presence of the best emulsifiers (77). When the system is in equilibrium with a gas phase, emulsification always occurs on irradiation, provided this pressure is neither too high nor too low. This very striking effect of the gas pressure is found without exception (76). According to Chambers and Gaines

(15) and Bondy and Sollner (77), the mechanism of emulsification in nonmetallic systems is as follows: A sound wave travelling through a liquid compresses and stretches it periodically. If the stretch is moderate and the irradiated liquid is free of gas, nothing spectacular occurs; but if the liquid is stretched unduly, even most carefully degassed liquids show zones of a slight and somewhat glittering opacity but no bubbles rise to the surface A hissing noise is always heard under these conditions (15, 52, 74, 77).

The glittering opacity indicates that the liquid disrupts and forms cavities under the stretch of the sound waves. High hydrostatic pressure prevents this disruption, and no hissing noise can be observed. *In vacuo*, even at low energies, the liquid bubbles and boils, and no hissing noise is heard. Under neither of these conditions does emulsification occur. Strong mechanical action caused by ultrasonics is always accompanied by a hissing noise. Obviously the formation of cavities alone does not cause emulsification; their disappearance under pressure, which is accompanied by a hissing sound, brings about the formation of emulsions (15, 74, 77).

The enormous local stresses and accelerations which occur when a vapor bubble collapses in a liquid (Rayleigh (63)) cause the intense mechanical effects. The entire phenomenon involving the formation of cavities and their violent collapse due to outside pressure is called "*cavitation.*" Cavitation occurs in an irradiated system preferentially at weak spots, where the energy of disruption is relatively low, as at oil–water interfaces (74, 77). We may visualize cavitation which leads to emulsification as a very violent hammering of the collapsing cavities, occurring at the phase boundary.

Before discussing emulsification and emulsions further, it seems appropriate to mention one more effect caused by the stretching of liquids and by cavitation. In liquids which are saturated with gas, cavitation is always accompanied by partial *degassing* (23). When the liquid is stretched and cavities are formed, some of the dissolved gas is obviously released into the latter; the cavities cannot collapse completely. Gas bubbles remain which, as we shall see below, unite readily under the influence of the sound waves into bigger ones and rise to the surface. Actually true cavitation, as described above, is not necessary for degassing; much weaker sound intensities are effective. Boyle (3, 4) is inclined to attribute this degassing to the presence of preformed gas nuclei; however, it seems more likely that the mechanism is as follows: When a sound wave passes through the liquid, the latter is stretched periodically; in this period it is supersaturated with respect to the gas, and minute gas bubbles are formed and coagulated.

We must break off the discussion of the degassing effect, which needs further careful experimental and theoretical investigation, and return to the problem of emulsification and *emulsions*.

Besides mercury, other metals may easily be dispersed if their melting points are low enough. They are dispersed only in the liquid state. In many cases stable truly colloidal solutions are obtained (81, 86). Solid metals cannot be dispersed merely by sonic irradiation.

Oil-in-water and water-in-oil emulsions can apparently be produced with any pair of incompletely miscible liquids, the limiting concentrations depending upon the nature of the system (79). In properly protected systems 75 per cent emulsions of oil in water are readily obtained.

The sonic methods of emulsification are undoubtedly very easy, convenient, and reproducible in studying emulsification and emulsions. Not the least of the advantages is that very small samples, as small as a drop, may be emulsified,—if necessary in sealed containers. On the other hand, large-scale operation is possible; Chambers (10, 11) has homogenized milk to induce soft curd character. With his electromagnetic sound generator and with a power input of 1 to 2 kilowatts, 250 gallons of milk per hour were treated successfully; with a magnetostriction sound generator at much lower rates of flow partial sterilization was also observed.

Mention must be made here also of the work by Masing and Ritzau (54), Schmid and Ehret (68), and others. *Dispersions of one* immiscible *metal in another* were prepared (lead in aluminum, calcium in silicon, etc.) by the application of intense sound waves to melts. The mechanism causing these dispersions is probably similar to the dispersion of mercury in water. It is claimed that these metal–metal dispersions have in the cooled state some highly desirable metallurgical properties, which are otherwise unobtainable. Further work along these lines seems to be highly desirable from the practical point of view.

The *formation of fogs*, i.e., the "atomization" of non-metallic liquids by ultrasonics (Wood and Loomis (86)) is best shown by irradiating a beaker containing some fairly volatile liquid with sound waves of high intensity. The beaker fills rapidly with a white cloud. With more viscous liquids special experimental arrangements must be used. The formation of fogs is due to the same mechanism as that causing emulsification in non-metallic systems, i.e., cavitation (73).

The *peptizing action of sound waves* on gels, gel-like substances, precipitates, and sediments has been extensively investigated. All such systems contain preformed particles of colloidal or semi-colloidal size. In all the numerous instances investigated so far it has been found that the primary particles may be separated from one another readily by cavitation caused by audible or inaudible sound waves (28). The preparations made by sound action do not show any special features; the sound waves act merely as a very efficient mechanical dispersing device.

The sound method of dispersion and peptization of sediments, precipitates, and gels undoubtedly offers many advantages on account of the cleanliness and good reproducibility of this method and the small quantities of materials necessary.

A case of special practical interest is the preparation of extremely fine-grained photographic emulsions of great sensitivity. Claus (17) and Dangers (20) irradiated silver bromide emulsions during their preparation. Claus reported in detail on the properties of these photographic preparations. The mechanism of the action of the sound waves in this case is not definitely known. One would be inclined to attribute it to cavitation. However, other suggestions have been made: the thermal effects associated with strong sound action (to be discussed below) and chemical activation (see below) (e.g., 62).

A *dispersion of solids in liquids* by sound methods can only be achieved with substances of moderate cohesion which are easily split and broken. This dispersion is due to cavitation. Materials comparatively easily dispersed in water, yielding colloidal or semi-colloidal solutions, are (crystals of) mica, gypsum, steatite, hematite, sulfur, and graphite (75). Some reports in the literature which claim the dispersion of metals and other substances of great cohesion have been shown to be based on faulty experiments.

The solid substance to be dispersed need not necessarily be of macroscopic size; even the particles of truly colloidal solutions may be broken down further by irradiation (75).

In order to circumvent in the case of metals the difficulties inherent in the dispersion of solids of great cohesion, Claus (18) and Claus and Schmidt (19; see also 84) submit systems to the action of strong ultrasonic waves in which metallic precipitates are simultaneously formed by electrolysis or chemical reaction. As cathode in the electrolysis process a non-corrosive metal, such as stainless steel, is used, to which the products of the electrolysis adhere poorly. The freshly formed metal is torn off the electrode (presumably by cavitation) and thus dispersed in the liquid. The authors cited report that they produced in this manner fine-grained dispersions of platinum, gold, silver, mercury, copper, cadmium, lead, bismuth nickel, chromium, iron, and aluminum. (The dispersions of the less noble metals are probably not of a purely "metallic" character.) The mercury emulsions produced by this method were much finer grained than those produced by dispersion of the bulk phase without electrolysis (19). There is little doubt that this method could be used to great advantage in many practical problems.

There are other electrode effects caused by sonic irradiation. Foremost among them is the *neutralization of passivity, and changes in electrode potentials,* both probably caused by the destruction of protecting layers.

In considering potentially useful applications of sonic dispersion, the straightforward *sonic extraction* method of Chambers and Flosdorf (14) for the preparation of labile bacterial constituents should be mentioned. By intense sonic irradiation bacteria in suspension are broken up and finally disintegrated completely (86); labile substances which are thereby released can thus be prepared in many cases, apparently without deterioration in their biological activity (14).

Changes in the anomalous viscosity of colloidal solutions, the splitting of macromolecules, and related phenomena caused by sound waves have been described frequently. One of the simplest and most easily understood cases is the reversible liquefaction of thixotropic gels (28, 30), the primary particles of these gels being loosened by cavitation. The liquefaction of thixotropic gels can be considered as an extreme case of change in anomalous ("structural") viscosity.

"Fluid" systems, the viscosity of which is decreased by sound waves, were first described by Szent-Györgi (83) and Szalay (83) (gelatin, starch, gum arabic). More thorough investigations of this problem were carried out by

Freundlich and Gillings (25) (gum tragacanth, gum arabic, gelatin, agar, cotton yellow, benzopurpurin, vanadium pentoxide, sodium stearate, and sodium oleate), and by Schmid and collaborators (67) (polystyrene, polyvinyl acetate, polyacrylic acid esters, nitrocellulose, rubber, etc.) (see also 21, 41, 66).

The solutions of gums show the simplest behavior. By short (0.5 to 3 min.) sonic treatment their viscosity and its anomalies are reduced: they become less viscous and show smaller deviations from Poiseuille's law. This effect is due to cavitation; on standing the viscosity rises gain, but full recovery does not occur (25).

With gelatin and agar solutions weak irradiation is sufficient to reduce the viscosity only at low shear rates; more intense irradiation effects an over-all reduction of viscosity at all shear rates. The solutions recover their structural properties rapidly on standing. If cavitation is rendered ineffective, the anomalous viscosity of gelatin solutions is much less affected by ultrasonic irradiation; however, some reduction in viscosity still occurs. Freundlich and Gillings think that in the region of lower shear rates the resistance of the solutions to flow is probably due to gel formation; at the higher shear rates we have a closer approach to a viscous resistance, the gel structure is destroyed, and the behavior is similar to that of a non-gelating solution, like a gum. Schmid and collaborators found a similar complexity of behavior in several other cases; they suggest that frictional forces resulting from the relative motions of a rigid network of macromolecules and the vibrating solvent may cause the breakdown of macromolecules (67). The degree and rate of recovery in such systems should be studied further; this problem blends gradually with that of influencing polymerization reactions.

Solutions of cotton yellow show distinct anomalous viscosity and strong streaming double refraction due to the presence of ultramicroscopic rod-shaped particles. Brief, low-intensity irradiation completely destroys (by cavitation) this anomalous viscosity, and the strong stream double refraction likewise disappears. There is but little recovery on standing. Ultramicroscopic examination after irradiation shows that the rod-shaped particles have disappeared, very fine, seemingly isotropic particles being present instead (25).

The viscosity of sodium stearate solutions is reduced rapidly by cavitation caused by intense ultrasonic irradiation; this is accompanied by a most marked change in appearance. Whereas the original solution has a curdy, opaque, somewhat gelated, but generally homogeneous appearance, the system after irradiation is a limpid suspension of silky, needle-shaped, crystalline particles, showing streaks of stirring. Ultrasonics in this case accelerate crystallization.

By irradiation with ultrasonics Brohult (8) has split hemocyanin into fragments of one-half and one-eighth their original size. Confirmation and expansion of this highly interesting observation seems most desirable. The denaturation of certain proteins by the action of sound (13, 53) in many cases seems to be due to a kind of surface denaturation.

III

After this outline of the disruptive and destructive effects of sonic and supersonic waves, which in most cases are caused by cavitation, we may turn now to their *ponderomotive action* and the phenomena which depend upon the latter.

The best-known ponderomotive effect of sound waves is the *accumulation* of fine solid particles in the nodes of a field of stationary sound waves *in gaseous systems*—Kundt's dust figures (51). The phenomenon is so well-known that a mere reference to figure 7 seems sufficient. In a sound field of ultrasonic frequency the phenomenon is much the same,—fine dust collects in the nodes.

FIG. 7. Kundt's dust figures in gases

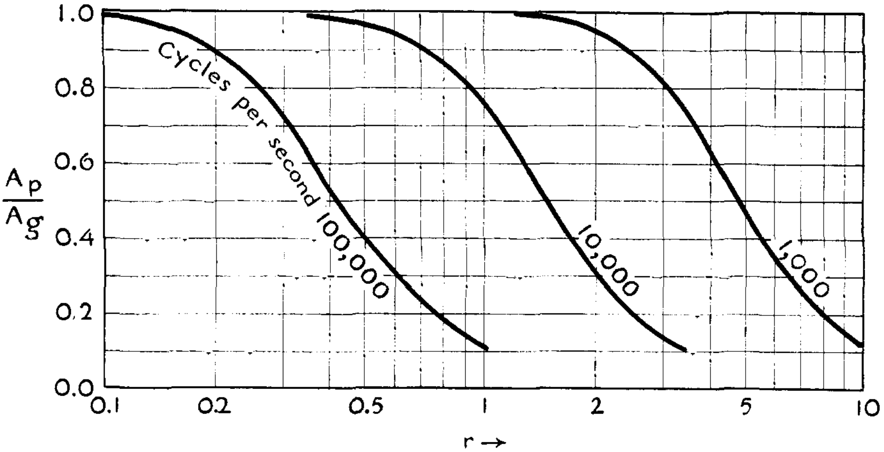

FIG. 8. The ratio of the amplitudes A_p/A_g in its dependence on particle radius (in microns) for different frequencies. (Curves calculated by H. Freund and E. Hiedemann)

The movements of the particles of an aerosol in a sound field are too complicated to be discussed quantitatively here. Suffice it to say that the individual particles of an aerosol follow the oscillations of the gaseous medium the more closely (*1*) the lower the frequency, (*2*) the smaller the mass of the particle, (*3*) the lower its density, and (*4*) the higher the viscosity of the gaseous medium. Small, light particles follow the movements of the medium almost completely at low frequencies; at higher frequencies this movement decreases as the frequency increases. Large particles oscillate but little even at low frequencies, their inertia being great compared with the forces acting upon them; they are practically stationary at high frequencies. Very instructive photographs of particles oscillating in a sound field were published by Brandt, Freund, and Heidemann (46). In the diagram of figure 8 are plotted the ratios of amplitudes of particle and gaseous carrier, A_p/A_g as a function of the particle radius, r, for these different frequencies, as calculated by Brandt, Freund, and Hiedemann (46). It is evident that with smoke and fog particles of the sizes that usually occur in natural and artificial smokes and fogs (0.5 tc 5 μ), the strongest effects can be expected in the region of sonic and lower ultrasonic frequencies.

The impulses received by the oscillating particles toward a node and away from it are not strictly symmetrical. The impulses from the side of the loops are slightly larger, since the loops are the places of the maximum movement of the oscillating gas. The net result of this asymmetry of oscillation is that the particles are slowly shifted toward the nodes, where they accumulate and aggregate (coagulate).

This *coagulation of aerosols* is without doubt the most intensively investigated action of sound waves in colloidal or semi-colloidal systems. Sonic coagulation in aerosols has been discussed by Patterson and Cawood (59), Pearson (60), Andrade and Parker (1, 58), Gottschalk and Clair (31), Clair (16), Brandt, Freund, and Hiedemann (6, 7, 42, 43, 44, 45, 46, 47), and many others.

In fogs and smokes practically all collisions between particles are non-elastic and lead to the formation of aggregates, i.e., they coagulate spontaneously. In view of the described oscillations and the accumulation of aerosol particles in a sound field it is not surprising that the coagulation of aerosols can be greatly accelerated if they are exposed to sound waves of higher acoustic or lower ultrasonic frequency.

The usual experimental set-up consists substantially of a cylindrical gas chamber, which is either filled with the aerosol, or, more advantageously, through which the aerosol flows continuously. The system is adjustable so that a stationary wave field may be set up; then the intensity of the sound field becomes many times that obtainable without this precaution, and rapid coagulation sets in, even in fast-flowing aerosols. Whereas under the proper conditions the untreated aerosols settle down as fine dust, mainly as primary particles, the sound-treated aerosols yield sediments composed of large aggregates. In many cases aggregation to a mass several thousand times that of the primary particles has been observed.

A quantitative theory of sonic coagulation is confronted with the greatest difficulties. In the process of coagulation, aerosols become very heterodisperse and the aggregates so formed deviate widely from a spherical shape. The worst difficulty is that the mechanism of coagulation is not simple, a number of not entirely independent factors working simultaneously to produce aggregation. The two main factors are hydrodynamic attraction between the oscillating particles and the increased probability of kinetic collisions between the particles oscillating with different amplitudes; the latter factor, as pointed out by Sollner (72), can be considered as a special case of orthokinetic coagulation (85). In addition, there are the changes in concentration and the spontaneous sedimentation of the aggregated particles which leads to orthokinetic coagulation, as originally conceived by Wiegner and collaborators (85) for liquid systems. The problem is so complex that a further discussion in this brief outline is impossible. The most up-to-date review has been given by Hiedemann (43).

Numerous attempts have been made to apply sonic coagulation methods to the precipitation of industrial fogs and smokes. Since coagulation occurs readily in streaming aerosols it is possible to handle large volumes; however, on the basis of the available literature no definite statement can be made at present as to whether or not sonic coagulation may be developed into an economical industrial method; the chances that this may be achieved seem to be rather good.

Accumulation in liquid systems: As in gaseous systems, accumulation occurs in liquids with dispersed gases, solids, and liquids, as described by Boyle *et al.* (4, 5). Sollner and Bondy (80) have investigated this accumulation more closely from the colloid chemical viewpoint. Stationary waves cause the formation of very beautiful and regular patterns—Kundt's dust figures (figure 9)—in liquids (76). With increasing time of irradiation the zones of accumulation may become very sharp; under favorable conditions thin discs with well-defined boundaries are seen in the liquid. The distance between two such bands is $\lambda/2$, λ being the wave length in the liquid. So far as experimental evidence shows at present, accumulation occurs at the nodes if the dispersed substance is less dense than the medium of dispersion, and at the antinodes if it is denser. In systems containing particles both denser and less dense than the dispersion medium, sound waves may separate the two kinds of particles from each other, the distance between a band of the one and the other being $\lambda/4$ (80).

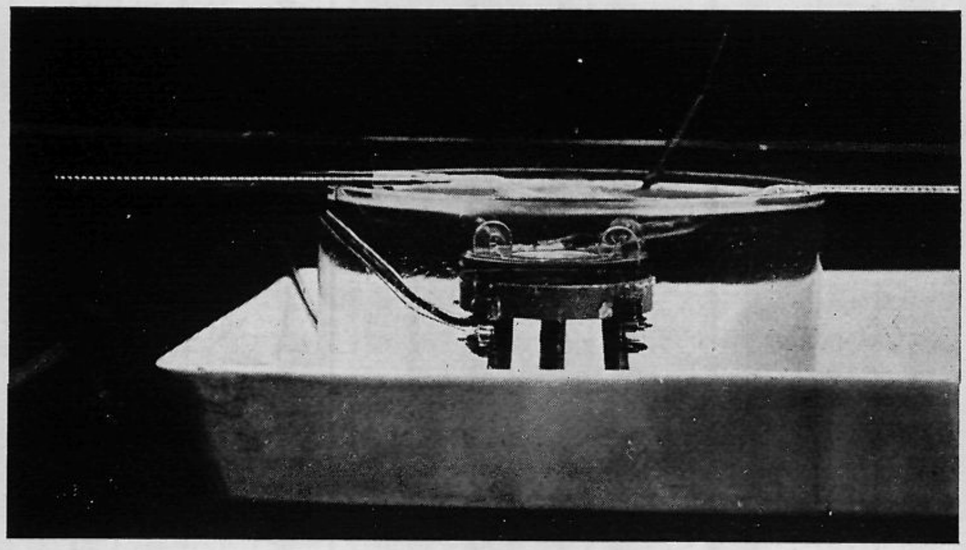

FIG. 9. Arrangement for the study of stationary wave patterns. About one-fourth actual size. (From K. Sollner and C. Bondy)

The rate of accumulation of dispersed substances at the nodes or antinodes depends on the size of the particles; very sharp wave patterns are formed immediately with particles of 4 to 10 μ. With particles of 1 μ and smaller, zones of diminished concentration appear after several seconds, but even after 30 min. the whole pattern is blurred. With particles of less than 0.5 μ, the effect is still less distinct. In truly colloidal solutions accumulation has not been obtained at all by Sollner and Bondy with a frequency of 214,000 cycles per second (80).

The theory of the ponderomotive action of sound waves has been discussed by Boyle (4, 5) and King (48); it is too complicated to be considered here.

Very closely linked to the accumulation effect is the *orientation of anisometric* *particles in liquid systems.* Sollner and Burger (82) found that anisometric particles are oriented in a sound field with their long axes perpendicular to the flux of energy. The phenomenon is best observed in a field of stationary waves. If a dilute suspension of mica, mosaic gold, certain clays, or similar materials is irradiated, silky, brilliantly glittering zones at half-wave distance appear immediately, a sure sign of orientation. The energy necessary to bring about orientation is very much smaller than that required for accumulation, the movement necessary for the former being only of the order of the length of the particles.

As in the case of accumulation, orientation also depends on the particle size, larger particles being much more readily oriented. Orientation (contrary to accumulation) can, however, be observed with truly colloidal solutions, as has been demonstrated with aged vanadium pentoxide and ferric oxide sols (82). Hermans (39), Oka (56), and others have investigated the orientation phenomenon further, and have tried to develop the physical theory of the effect, mainly on the basis of theoretical considerations of King (48).

The *coagulating action of sound waves in liquid systems* containing macroscopic particles on the one hand and truly colloidal solutions on the other seems to be due to entirely different mechanisms; the two cases must therefore be treated separately.

The *coagulation in liquid systems with visible or micrscopic particles* can be demonstrated very strikingly by irradiating unstable suspensions, e.g., quartz powder in an organic liquid. If such a suspension is irradiated even with low sound intensities, the particles accumulate and aggregate readily; the aggregates so formed soon reach a size which favors rapid sedimentation. A few seconds of weak irradiation are sufficient to clear the suspended particles from the liquid. Very similar is the coagulation of gas bubbles in liquids, whether they are preformed or are generated in the system by sound waves, as discussed above.

In a less spectacular manner the same result is obtained with more stable emulsions and suspensions. The coagulation always occurs in the zones of accumulation in the liquid (figures 10, 11a, and 11b). With oil emulsions cavitation must be prevented. Longer application of sound causes in emulsions not only aggregation but also coalescence; emulsions may be broken completely (figure 11b). With highly protected emulsions the particles aggregate, but coalescence occurs only extremely slowly; the aggregates may easily be redispersed. The same, of course, is true for highly charged, stable suspensions.

Qualitatively, Sollner and Bondy (80) explain the coagulating action of sound waves in systems with microscopic particles in this manner: (*1*) the particles are accumulated and the rate of spontaneous coagulation increases rapidly as the concentration increases; (*2*) particles of different size migrate with different velocities toward the zones of accumulation, thus being liable to additional collisions, a kind of "orthokinetic" coagulation (85); (*3*) the asymmetry of the oscillations which the particles perform according to their (different) size causes additional collisions. Whether the factors enumerated completely explain the phenomena is still open to question; it is possible that hydrodynamic attraction between oscillating bodies (see, e.g., reference 57) in the zones of accumulation comes into play, as may also dipole forces which are believed (40) to be the most important single factor with truly colloidal solutions.

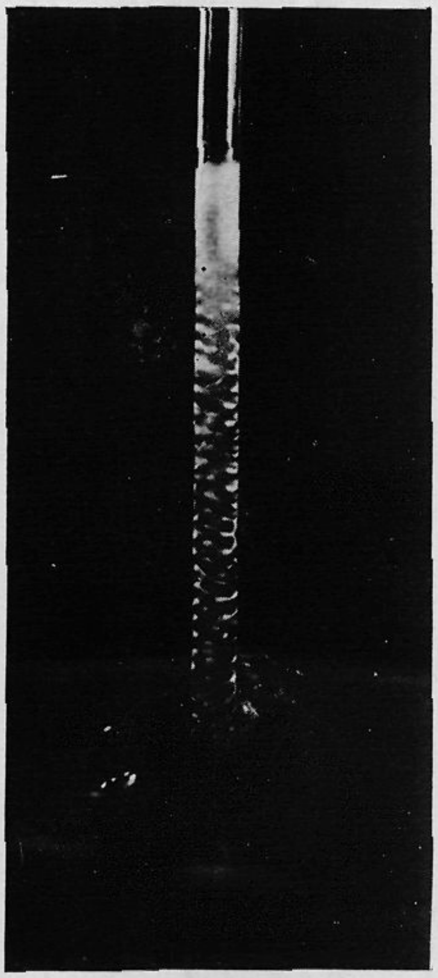

FIG. 10. Coagulation of an emulsion by ultrasonics. About one-quarter actual size. (From K. Sollner and C. Bondy)

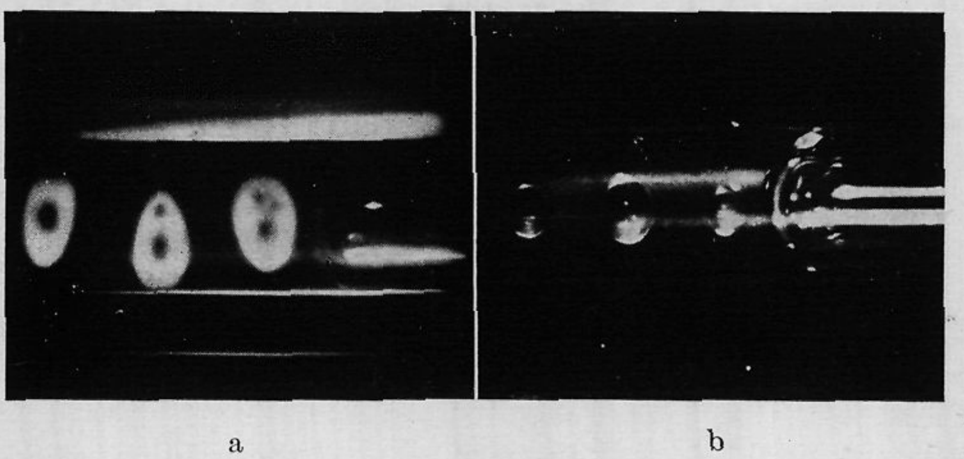

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FIG. 11. Coagulation of an emulsion: the formation of oil drops in the zones of accumulation (a) after brief sonic treatment and (b) after prolonged sonic treatment. (From K. Sollner and C. Bondy)

It seems not improbable that sonic coagulation in systems with macroscopic and microscopic particles may assume some technical importance in the future. Several years ago we (30) suggested the removal of the gas bubbles from the very viscous technical viscose solutions. The degassing of metallic melts and of glasses was tried by Krüger (50) and others (e.g., 49). In all these cases the useful process is more a coagulation of preformed gas bubbles than a true degassing. The breaking of crude oil emulsions is also mentioned in the patent literature.

Coagulation in truly *colloidal solutions* may be brought about by the action of sound. The mechanisms involved, however, must of necessity be of a different nature, since the ponderomotive effects responsible for the coagulation in systems with microscopic particles are practically absent, as pointed out above. Hermans has investigated the problem theoretically (38), as well as experimentally (40), with dilute silver iodide sols. The very slow rate of spontaneous coagulation in these sols is hardly influenced by sound treatment. In the presence of electrolytes—ammonium chloride, sodium nitrate, potassium nitrate (0.6–0.24 M), and barium chloride (0.001–0.02 M)—the rate of coagulation is increased in a sound field of moderate or high energy. This influence is very pronounced at low electrolyte concentrations, that is, in the range of "slow coagulation"; it is almost negligible at high electrolyte concentrations, where the coagulation is rapid. Hermans thinks that neither heat effects, the kinetic energy of oscillations, nor orthokinetic coagulation, accumulation, nor hydrodynamic interaction between the particles can account for the observed facts. He sees the most promising explanation in the dipolar interaction of the oscillating particles ("migrating dipoles"), which results from the distortion of the electric double layer surrounding the individual particles. This problem seems to be still far from a definite solution; much more experimental work with a variety of sols is needed.

Closely related to the phenomenon of accumulation in systems with microscopic particles is the acceleration of *solidification in* certain *rheopectic systems* which can be brought about by sound waves. The time of solidification of certain types of thixotropic systems is shortened by submitting them to a more or less regular movement, such as tapping the test tube containing the sol or slowly rolling it to and fro between the palms of the hands. This phenomenon is called *rheopexy* (27). Rheopectic solidification can be brought about by treatment with sound in those rheopectic systems which are more paste-like than gel-like, and whose particles are big enough to be influenced—by being either oriented or translocated—individually by the sound waves (82).

The last of the effects caused by the ponderomotive *action of sound waves* is their influence *in dilatant systems* (82). If the supernatant liquid is poured off the sediments of certain suspensions, such as quartz powder or sea sand, the sediments are somewhat moist and soft when only a slight pressure is applied. However, as soon as a stronger, one-sided pressure is applied, a sediment of this kind becomes dry and hard and offers considerable resistance to a penetrating instrument; as soon as the pressure ceases, the whole mass usually becomes moist again. This phenomenon is called dilatancy (64). In moist sand the particles tend to become very closely packed. If an external force displaces the particles, the packing becomes looser and consequently water is sucked in, thus leaving the sediment apparently dry and hard. When a system normally exhibiting dilatancy is exposed to ultrasonics it is possible to drive an instrument through the sand without much resistance. It seems to hold true generally that dilatant and, therefore, non-plastic systems can be rendered somewhat plastic for the duration of intense sound treatment (82). This effect may become of some interest in drilling and molding operations.

All the described effects caused by intense sound treatment in liquid and solid systems are always accompanied by considerable *heat development* (30, 86). This thermal effect is particularly pronounced in the presence of extended phase boundaries, as they occur in microheterogeneous systems. Temperature increases in irradiated liquid samples of up to 1°C. in 3 sec. have been reported. Rises of 5 to 10°C. in temperature are common and are usually unavoidable when studying emulsification, etc.

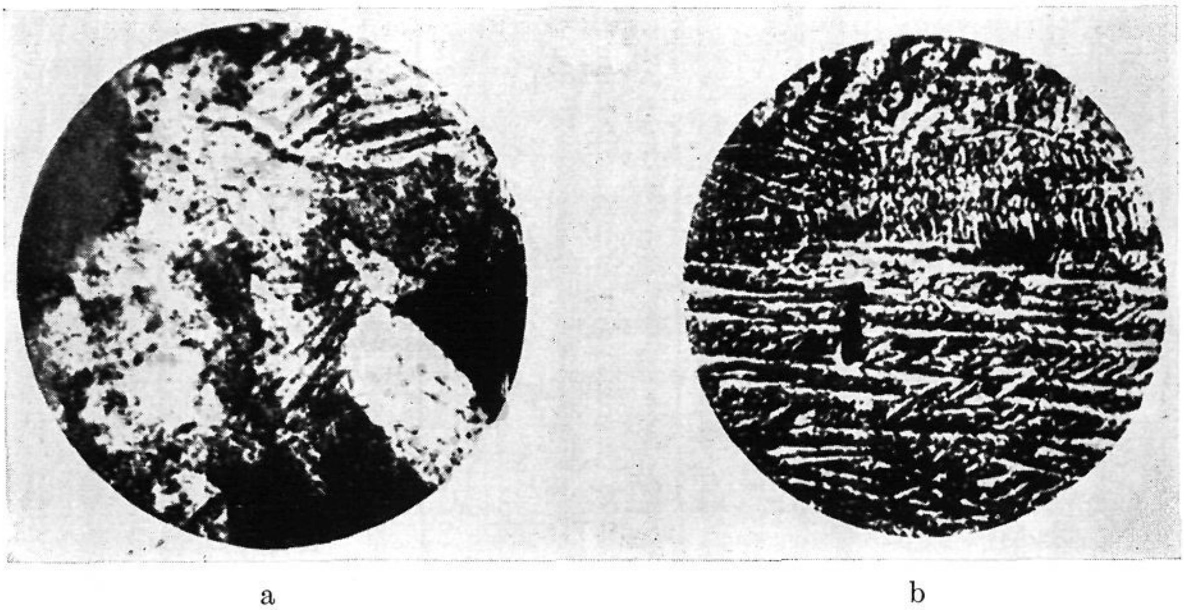
a b

FIG. 12. The crystallization of zinc (a) without a sound field and (b) in a sound field. (From S. J. Sokoloff)

The heat effect is due to a number of factors, the relative importance of which depends on the system under consideration: absorption, gross stirring, the irregular reflection and the scattering of sound on interfaces, the friction between the particles and the oscillating dispersion medium, cavitation, etc. A detailed investigation of the heat effect in heterogeneous systems has never been carried out. The unavoidable heat development is a rather disturbing factor in many investigations, particularly in the range of ultrasonic frequencies. It has been suggested (29) that one might use it for medical purposes, such as the heating of joints, of the marrow inside intact bones, etc.

A discussion of the *chemical action of sound waves* is outside the framework of this review and can be referred to only briefly.

Schmitt, Johnson, and Olson (70) first showed that strong ultrasonic irradiation of water containing oxygen leads to the formation of hydrogen peroxide. This, as established later, is due to the activation of oxygen by the collapse of cavities.

In the presence of suitable reagents the activated oxygen, of course, may bring about many varied secondary oxidation reactions. The activation of oxygen is accompanied by the emission of light (sonoluminescence). The problem of sonic oxidation and sonoluminescence has been reviewed by Harvey (36).

Sound action may frequently change *labile states* to more stable ones. Such effects as the sudden boiling of superheated liquids or the detonation of highly sensitive explosives when subjected to sound waves (86) do not require further comment. Of interest here is the *spontaneous crystallization* from supersaturated solutions which frequently occurs (86) and which probably has considerable metallurgical importance (9, 24, 68, 69, 71); its mechanism is unknown. The crystalline structure of metals and alloys is changed by sonic treatment of their melts during solidification; the grain size is generally reduced and the growth of dendrites sometimes favored (figure 12). The results of different authors still vary widely, probably owing to differences in the systems investigated and the sound frequencies used.

A few general remarks must suffice for the *biological effects of sound.* In view of the disruptive and destructive, ponderomotive, and chemical actions of intense sound, it is small wonder that living systems are affected greatly by intense sound treatment. A very great number of observations have been reported. The reader is referred to the work of Harvey and collaborators (34, 35, 37), Chambers and collaborators (12, 14), and to the reviews of Dognon, Biancini, and Biancani (22) and Hiedemann (43).

SUMMARY

Ultrasonic (inaudible) and sonic (audible) sound waves alike bring about many phenomena of interest to the colloid chemist. They cause on the one hand all kinds of disruptive and destructive phenomena, such as emulsification, peptization, dispersion of certain solids in liquids, formation of fogs, etc.; on the other hand, they bring about orientation, accumulation, aggregation, and coagulation in liquid and gaseous colloidal and semi-colloidal systems.

The different methods of producing high-intensity sound waves are critically sketched, and the various mechanisms which cause these above-mentioned phenomena are reviewed.

Certain instances of possibly useful applications of sound waves are given. Sound waves offer a very convenient method for the study of emulsification and emulsions; emulsions may be produced or homogenized, and they may also be broken. Unstable suspensions may be coagulated. Sound waves further allow the colloidal dispersion of many metals in aqueous solutions, by the use of the Claus electrolytic method; also very fine grained photographic emulsions of great sensitivity can be produced. Immiscible metals may be dispersed in each other.

Sound waves may become a valuable tool in studying gels and systems showing anomalous viscosity.

Some proteins are denatured by sound waves; some are split to form seemingly well-defined fragments.

The coagulation of smokes and fogs by sound, though of an extremely complicated nature, seems to promise wide technical application.

Another useful application may come from the effect of sound waves on the structure of metals and alloys, when applied during their crystallization, and possibly also from the degassing action of sound on glasses and metallic melts.

The author wishes to thank the editor of the *Transactions of the Faraday Society* for permission to use freely his papers published therein and to reproduce a number of photographs; Dr. Jerome Alexander and the Reinhold Publishing Corporation, New York, for permission to use figures from an article by the author on "Sonic and Ultrasonic Waves in Colloid Chemistry", which is to be published in Volume V of Jerome Alexander's *Colloid Chemistry: Theoretical and Applied;* and the editors of the *Proceedings of the Society for Experimental Biology and Medicine* and Dr. L. A. Chambers for permission to reproduce figure 4.

REFERENCES[1]

(1) ANDRADE, E. N. DA C.: Trans. Roy. Soc. (London) **A230**, 413 (1932); Trans. Faraday Soc. **32**, 1111 (1936).
(2) BERGMANN, L.: *Ultrasonics and their Scientific and Technical Application* (translated by H. Stafford Hatfield), Bell and Sons, Ltd., London (1938); *Der Ultraschall und seine Anwendung in Wissenschaft und Technik*, 2nd edition, VDI-Verlag, Berlin (1939).
(3) BOYLE, R. W.: Trans. Roy. Soc. Can. [3] **16**, 157 (1922).
(4) BOYLE, R. W.: Science Progress **23**, 75 (1928).
(5) BOYLE, R. W., AND LEHMANN, J. F.: Trans. Roy. Soc. Can. **19**, 159 (1925).
(6) BRANDT, O.: Z. physik. chem. Unterricht **50**, 1 (1936); Kolloid-Z. **76**, 272 (1936).
(7) BRANDT, O., AND FREUND, H.: Z. Physik **92**, 385 (1934); **94**, 348 (1935).
(8) BROHULT, S.: Nature **140**, 805 (1937).
(9) CEROVSKA, J.: Strojnický Obzor **19**, 145; 185 (1939).
(10) CHAMBERS, L. A.: J. Dairy Sci. **19**, 29 (1936).
(11) CHAMBERS, L. A.: Certified Milk, November (1939).
(12) CHAMBERS, L. A.: J. Biol. Chem. **117**, 639 (1937).
(13) CHAMBERS, L. A., AND FLOSDORF, E. W.: J. Am. Chem. Soc. **55**, 3051 (1933); J. Bact. **31**, 570 (1936); J. Biol. Chem. **114**, 75 (1936).
(14) CHAMBERS, L. A. AND FLOSDORF, E. W.: Proc. Soc. Exptl. Biol. Med. **34**, 631 (1936).
(15) CHAMBERS, L. A., AND GAINES, N.: J. Cellular Comp. Physiol. **1**, 451 (1932).
(16) CLAIR, H. W. ST.: U. S. Bur. Mines, Repts. Investigations **3400**, 51 (1938); Conf. Met. Res. Met. Div., Bur. Mines (Salt Lake City), p. 99, May (1940).
(17) CLAUS, B.: Z. tech. Physik **15**, 74 (1934); **16**, 109 (1935).
(18) CLAUS, B.: Z. tech. Physik **16**, 80 (1935); **16**, 202 (1935).
(19) CLAUS, B., AND SCHMIDT, E.: Kolloid-Beihefte **45**, 41 (1936).
(20) DANGERS, H. W.: Z. Physik **97**, 34 (1935).
(21) DEMANN, W., AND ASBACH, H. R.: Tech. Mitt. Krupp **3**, 12 (1940).
(22) DOGNON, A., BIANCANI, E., AND BIANCANI, H.: *Ultra-Sons et Biologie*. Gauthier-Villars, Paris (1937).
(23) DÖRSING, K.: Ann. Physik [4] **25**, 227 (1908).
(24) FÖRSTER, F., AND SCHEIL, E.: Z. Metallkunde **28**, 245 (1936).

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[1] An extensive review of the subject of sonic and ultrasonic waves in colloid chemistry by the author will be published in Volume V of Jerome Alexander's *Colloid Chemistry: Theoretical and Applied*, Reinhold Publishing Corporation, New York (in press).

(25) Freundlich, H., and Gillings, D. W.: Trans. Faraday Soc. **34,** 649 (1938).
(26) Freundlich, H., and Gillings, D. W.: Trans. Faraday Soc. **35,** 319 (1939).
(27) Freundlich, H., and Juliusburger, F.: Trans. Faraday Soc. **31,** 920 (1935).
(28) Freundlich, H., and Sollner, K.: Trans. Faraday Soc. **32,** 966 (1936).
(29) Freundlich, H., Rogowski, F., and Sollner, K.: Klin. Wochschr. **11,** 1512 (1932).
(30) Freundlich, H., Rogowski, F., and Sollner, K.: Kolloid-Beihefte **37,** 223 (1933).
(31) Gottschalk, V. H., and Clair, H. W. St.: Mining and Met. **18,** 224 (1937).
(32) Gruetzmacher, J.: Z. Physik **96,** 342 (1935); Z. tech. Physik **17,** 166 (1936).
(33) Hartmann, J.: Physiol. Rev. [2] **20,** 114; 719 (1922); Verh. 3, Intern. Kongr. tech. Mech., Stockholm, **3,** 329 (1931); Phil. Mag. [7] **11,** 926 (1931); J. phys. radium [7] **2,** 49 (1936).
(34) Harvey, E. Newton: Am. J. Physiol. **91,** 284 (1929).
(35) Harvey, E. Newton: Biol. Bull. **59,** 306 (1930).
(36) Harvey, E. Newton: J. Am. Chem. Soc. **61,** 2392 (1939).
(37) Harvey, E. Newton, and Chambers, L. A.: J. Morphol. **52,** 155 (1931).
(38) Hermans, J. J.: Phil. Mag. **25,** 426 (1938); **26,** 674 (1938); Rec. trav. chim. **58,** 164 (1939).
(39) Hermans, J. J.: Rec. trav. chim. **57,** 1349 (1938).
(40) Hermans, J. J.: Rec. trav. chim. **58,** 139 (1939).
(41) Heymann, E.: Trans. Faraday Soc. **31,** 846 (1935).
(42) Hiedemann, E.: Kolloid-Z. **77,** 168 (1936); Trans. Faraday Soc. **32,** 1120 (1936).
(43) Hiedemann, E.: *Grundlagen und Ergebnisse der Ultraschallforschung.* W. de Gruyter and Co., Berlin (1939).
(44) Hiedemann, E., and Brandt, O.: Kolloid-Z. **75,** 129 (1936); Trans. Faraday Soc. **32,** 1101 (1936).
(45) Hiedemann, E., Brandt, O., and Freund, H.: Kolloid-Z. **77,** 103 (1936).
(46) Hiedemann, E., Brandt, O., and Freund, H.: Z. Physik **104,** 511 (1937).
(47) Hiedemann, E., Brandt, O., and Freund, H.: Verhandl. deut. physik. Ges. [3] **18,** 28 (1937).
(48) King, L. V.: Proc. Roy. Soc. (London) **A147,** 212 (1934); **153,** 1 (1935).
(49) Klein, V.: Glastech. Ber. **16,** 232 (1938).
(50) Krüger, F.: Glastech. Ber. **16,** 233 (1938).
(51) Kundt, A.: Pogg. Ann. Physik. **127,** 497 (1866); **128,** 337, 496 (1866).
(52) Kundt, A., and Lehmann, O.: Pogg. Ann. Physik **153,** 1 (1874).
(53) Liu, Szu-Chih, and Wu, Hsien: Proc. Soc. Exptl. Biol. Med. **28,** 782 (1930).
(54) Masing, G., and Ritzau, G.: Z. Metallkunde **28,** 293 (1936).
(55) Nordlund, I.: Kolloid-Z. **26,** 121 (1918); Dissertation, Upsala, 1918.
(56) Oka, S.: Kolloid-Z. **87,** 37 (1939); Z. Physik **116,** 632 (1940).
(57) Oseen, C. W.: *Hydrodynamik.* Leipzig (1927).
(58) Parker, R. C.: Trans. Faraday Soc. **32,** 1115 (1936); Proc. Phys. Soc. (London) **49,** 95 (1937).
(59) Patterson, H. S., and Cawood, W.: Nature **127,** 667 (1931).
(60) Pearson, E. B.: Proc. Phys. Soc. (London), **47,** 136 (1935).
(61) Pierce, G. W.: Proc. Am. Acad. Arts Sci. **63,** 1 (1928); Proc. Inst. Radio Engrs. **17,** 42 (1929); J. Acoust. Soc. Am. **9,** 185 (1938).
(62) Protas, I. R.: Kinofotokhim. Prom. **1,** 38(1940); **5,** 43 (1940).
(63) Rayleigh, Lord: Phil. Mag. [6] **34,** 94 (1917).
(64) Reynolds, Osborne: Phil. Mag. [5] **20,** 469 (1885); Nature **33,** 429 (1886).
(65) Richards, W. T.: J. Am. Chem. Soc. **51,** 1724 (1929).
(66) Sata, N.: Kolloid-Z. **88,** 182 (1939).
(67) Schmid, G.: Z. physik. Chem. **A186,** 113 (1940); Physik. Z. **41,** 326 (1940).
Schmid, G., and Rommel, O.: Z. physik. Chem. **A185,** 97 (1939); Z. Elektrochem. **45,** 659 (1939); etc.
(68) Schmid, G., and Ehret, L.: Z. Elektrochem. **43,** 869 (1937).

(69) Schmid, G., and Roll, A.: Z. Elektrochem. **45**, 769 (1939); **46**, 653 (1940).
(70) Schmitt, F. O., Johnson, C. H., and Olson, A. R.: J. Am. Chem. Soc. **51**, 370 (1929).
(71) Sokoloff, S. J.: Acta physicochim. U. R. S. S. **3**, 939 (1935).
(72) Sollner, K.: Trans. Faraday Soc. **32**, 1119 (1936).
(73) Sollner, K.: Trans. Faraday Soc. **32**, 1532 (1936).
(74) Sollner, K.: Trans. Faraday Soc. **32**, 1537 (1936).
(75) Sollner, K.: Trans. Faraday Soc. **34**, 1170 (1938).
(76) Sollner, K.: J. Phys. Chem. **42**, 1071 (1938).
(77) Sollner, K., and Bondy, C.: Trans. Faraday Soc. **31**, 835 (1935).
(78) Sollner, K., and Bondy, C.: Trans. Faraday Soc. **31**, 843 (1935).
(79) Sollner, K., and Bondy, C.: Trans. Faraday Soc. **32**, 556 (1936).
(80) Sollner, K., and Bondy, C.: Trans. Faraday Soc. **32**, 616 (1936).
(81) Sollner, K., and Bull, H. B.: Kolloid-Z. **60**, 263 (1932).
(82) Sollner, K., and Burger, F. J.: Trans. Faraday Soc. **32**, 1598 (1936).
(83) Szent-Györgi, A.: Nature **131**, 278 (1933).
Szalay, A.: Z. physik. Chem. **A164**, 234 (1933); Physik. Z. **35**, 293 (1934).
(84) Urazovskiĭ, S. S., and Polotskiĭ, I. G.: Colloid J. (U. S. S. R.) **6**, 779 (1940).
(85) Wiegner, G.: Z. Pflanzenernähr. Düngung Bodenk. **A11**, 185 (1928); J. Soc. Chem. Ind. **50**, 55 (1931); Kolloid-Z. **58**, 157 (1932).
Müller, H.: Kolloid-Beihefte **27**, 223 (1928).
Tuorila, P.: Kolloidchem. Beihefte **24**, 1 (1927).
(86) Wood, R. W., and Loomis, A. L.: Phil. Mag. [7] **4**, 417 (1927).