of the rate equation is so great as to make such a determination impossible. On the other hand, if the concentration of the ferrous salt is made large, the retarding effect of the resulting ferric ion, which was observed by Winther, will be large in comparison to k_6. When the concentration of oxygen is large, k_6 and the first term of the equation may be neglected. Under these conditions the oxygen cancels out of the second term and the rate is independent of the oxygen concentrations.

The discussion of the mechanism of the chains occurring in these reactions will be postponed until more work has been done on the reaction in acid solution and on the photochemical reaction.

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THE CHEMICAL EFFECTS OF HIGH FREQUENCY SOUND WAVES
II. A STUDY OF EMULSIFYING ACTION

BY WILLIAM T. RICHARDS

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One of the most spectacular manifestations of the effects of the high frequency sound waves produced by Wood and Loomis[1] is their emulsifying action on benzene, paraffin and even mercury in contact with water. Since this action promises to be of some practical value and since, moreover, it gives important indications of the nature of sound wave effects, it has been briefly investigated.

1. **The Mutual Emulsification of Two Liquids.**—When benzene and water are placed in a test-tube which has been previously wet with water and the tube is irradiated with intense sound waves of 300 K.C., the benzene layer at once becomes cloudy, the water layer more slowly so and, finally, the boundary between the two disappears. A similar action may be observed between water and any other liquid of similar physical properties; even medicinal paraffin follows the same course. With high intensities of sound the agitation of the interface is, however, so intense that reliable observation of the locality at which emulsification occurs is impossible.

In order to verify the suspicion that emulsifying action occurs primarily at the wall in contact with benzene and not at the liquid–liquid interface, very low intensities of sound (roughly one-tenth of those employed by Wood and Loomis, and the author and Loomis,[2] and designated by the latter 100%) were used, and the following results obtained.

In water-wet tubes containing a benzene–water interface the white

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[1] R. W. Wood and A. L. Loomis, *Phil. Mag.*, [vii] **4**, 417 (1927).

[2] W. T. Richards and A. L. Loomis, THIS JOURNAL, **49**, 3086 (1927).

cloud of emulsion came off the walls of the tube slowly into the benzene layer only. There was little agitation of the interface, and the water layer remained clear until, after two minutes, when the benzene layer was extremely milky, a thin but gradually increasing haze of emulsion drifted down from the interface.

In dried test-tubes into which water was pipetted with great care to avoid wetting the upper part of the tube, and benzene then similarly added, no emulsification whatever took place unless the sound wave intensity was sufficient to agitate the interface considerably. Then emulsion formed at the wall-layer so produced, and was slowly driven through the liquid by radiation pressure. If drops of water were attached to the wall opposite the benzene layer they became milky and gradually emulsified completely. The converse was also true.

These results were verified with many immiscible liquids, a uniform indication being obtained with all. At low intensities of sound, emulsification evidently takes place almost wholly at the wall in contact with the dispersion medium when wetted with the liquid dispersed.

An attempt was made to study the action of sound waves on a benzene–water interface when confusing wall action was eliminated by damping out as far as possible vibrations in the glass. For this purpose a vessel was made consisting of a wide glass tube to the bottom of which was cemented a brass collar and a very thin brass membrane. Further to damp vibrations in the glass it was wound with heavy layers of rubber bands immediately above and below the benzene–water interface. When radiated with sound care was taken to immerse only the brass collar in the oil transmitting sound waves from the vibrating crystal since, brass being a poor conductor of transverse waves, the greater part of the sound energy present in the tube must then enter the liquid through the metal membrane. Under these conditions no visible action took place at the interface, although with very high intensities of sound slow emulsifying action at the walls was noted. This is a further indication that the major part of the emulsifying process occurs at the wall.

The type of emulsion produced when mercury is dispersed in water demands another explanation, since mercury does not wet the glass tube. It has never been found possible, moreover, to cause the mutual solution of the mercury and water layers. In this case the action, if studied under varying conditions, takes place somewhat differently. It is dependent, in the first place, on the amount of mercury in the tube. If 1 cc. is present in a pyrex combustion tube with 10 cc. of water, emulsifying action proceeds rapidly. If 2 cc. of mercury is present it proceeds more slowly, and with 5 cc. of mercury it is almost completely arrested even with the highest sound wave intensity. This may safely be attributed to the damping action of the mercury on waves in the glass. When under the best conditions for observation the emulsifying action may be seen to take place only in a small ring where the mercury, water and glass are in contact. Then white ribbons of emulsion are driven out slowly into the water from this circle. The action is accelerated by ammonium chloride, which is a pronounced emulsifying agent. Mercury withdrawn from sound action in water-wetted tubes and quickly strained through filter paper has an abnormally high water content, which it soon loses; it is therefore probable that water is emulsified in mercury, although the emulsion soon stratifies.

A picture of the mechanism of this emulsification may readily be formed on the basis of these results. It evidently is closely parallel to that described by Nordlund,[3] who obtained similar emulsions by bubbling water through a mercury layer.

2. **Emulsification as a Measure of Sound Wave Intensity.**—When this investigation was undertaken it was hoped that an absolute measure of local forces in the sound waves producing emulsification could be obtained. There remains, however, a certain usefulness for the emulsification process as a measure of relative sound intensities.

The following method makes this possible and gives, moreover, certain other valuable indications. Uniform test-tubes were coated internally with a mixture of celluloid and medicinal paraffin dissolved in acetone of such composition that, on the evaporation of the acetone and after drying for two hours at 70°, a coherent mixed film was formed which did not either peel or release paraffin on the introduction of water into the tube. By raying these tubes and measuring nephelometrically their turbidity, a standard of radiation intensity was obtained which was reproducible to about 20%.

The emulsification in these tubes, since it proceeded under almost optimal conditions, made possible the detection of exceedingly small intensities of sound. Only certain isolated spots on the glass surface were active in the process and ribbons of emulsified oil were shot from them across the tube. More emulsification took place at the top of the tube, which was open and hence relatively undamped, than at the bottom, which was necessarily immersed in oil.

3. **The Emulsification of Glass in Water.**—The intense emulsifying action at the wall of a glass vessel raises the question whether glass itself is emulsified on prolonged radiation. In more general investigations in progress with sound waves it is important to answer this and to ascertain with some precision the alteration of the properties of water if any occurs.

To this end pyrex tubes were washed with soap and water, heated with chromic acid and nitric acid and finally boiled repeatedly with distilled water. They were then filled by distillation without ebullition, being

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[3] Nordlund, "Dissertation," Upsala, **1918**.

washed with the water so distilled repeatedly until no further dust particles could be observed in the liquid. They were then sealed off without admission of air. In this way water was obtained showing only a faint uniform blue cone, due probably to the molecular scattering of water, with intense illumination and a black background.

One of these tubes was rayed with maximum intensity for sixty minutes. It showed a distinct increase in turbidity in an intense Tyndall beam, indicating that a small amount of glass had been torn from the sides, but the change in turbidity was not detectible with a precision nephelometer. By a dielectric loss method to be described elsewhere it was demonstrated that the electrolyte concentration was less than 10^{-6} N. The P_{H}, as measured by bromthymol blue, was about 0.2 units more basic than that in an unrayed tube, but this was not considered significant in unbuffered water. Five cc. of the liquid from the rayed and from an unrayed tube evaporated on a watch glass showed that the former had a slightly greater non-volatile content, but the difference was too small to be detectible on a precision analytical balance.

Since the result was clearly negative, except in so far as slight fragmentation of the sides of the tube was concerned, and since raying for an hour is a tedious matter, no further experiments of a similar nature were carried out.

These results make it appear unlikely that sound waves should in a liquid fracture small glass particles. This supposition was confirmed by experiment. Uniform glass particles which would pass an 80 to the inch but not pass a 100 to the inch sieve were selected, washed with chromic acid, and violently agitated many times with distilled water. Particles of this size were too small, if in low concentration, readily to undergo flocculation by the sound waves, and yet not small enough to be held in standing waves at the glass surface and thus suffer possible mechanical fracture. A standard weight of glass in water was rayed for unit intervals of time and an identical weight was simultaneously given violent mechanical agitation in another portion of water of the same volume. After raying, the water from the two was poured off and compared nephelometrically. The turbidity of both converged toward the same limit within error of measurement, indicating that, although patently more effective in detaching adhering smaller particles of glass, the sound waves were causing no more actual breakage of the larger particles than that which mechanical agitation produced.

Discussion

The observations recorded above indicate clearly that emulsification in a liquid takes place largely at the walls of the containing vessel when they are wetted with the liquid dispersed. This makes it improbable that compressional waves in the liquid produce the action; more probably the transverse waves in glass, noted by Wood and Loomis, are the effective agents. As described by these authors the transverse waves in a glass rod 0.1 mm. in thickness at a frequency of 300 K.C. have a wave length of about 6 mm., which gives an index to the general characteristics of similar waves in a test-tube of equal thickness. Their amplitude, as judged by their physical effects, must be far larger than that of the compressional waves in the same medium; measured under somewhat different conditions it was of the order of 6000 Å.

This conclusion makes it appear probable that many destructive phenomena, which have formerly been attributed to direct action of the sound waves in liquids, are, in fact, of a secondary nature. The rupture of blood cells, small unicellular organisms, and the like cannot now necessarily be supposed to take place in the liquid proper, but may evidently occur primarily in the neighborhood of the walls.[4] Any small body perceptibly adsorbed by the glass surface would, of course, be even more subject to this destructive action. Indeed, in all cases where sound is transmitted through a glass vessel into a liquid, transverse waves must be considered as a possible primary explanation for any effects observed. Action on dry explosives and liquid-in-air cloud production may safely be attributed to the same cause in most cases.

These data, furthermore, indicate clearly the method by which emulsification may be most effectively produced in any desired case. It is evidently unnecessary to have a liquid–liquid interface in the containing vessel except as an envelop for the dispersion medium. The same considerations, with obvious modification, apply equally to solid-liquid systems.

Finally, it follows that no measurements valuable for the estimation of the absolute radiation pressure in a liquid can be obtained from a study of emulsification. The effects of transverse wall waves must inevitably be confused with the effects of compressional waves in the liquid. Furthermore, even if, at high intensities, emulsification occurred at a plane liquid–liquid interface, it would not be amenable to quantitative treatment. The process of emulsification is, in such a case, a matter essentially of velocity and not of equilibrium: in order to be perceptible a definite amount of liquid must be dispersed in a given time. The radia-

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[4] This statement must not be considered categorical. Turtle's blood is laked, although slowly, in a rubber bag in which transverse waves connot exist. Certain phenomena encountered in the capillary of a funnel gage [W. T. Richards, *Proc. Nat. Acad. Sci.*, **15**, 310 (1929)], where the sound energy is concentrated by reflection, indicate that fracture of a liquid–liquid surface may take place in the absence of transverse waves. The fracture of a gas–liquid interface by compressional waves in the liquid is evidently far easier. This is demonstrated strikingly at high sound intensities by the emergence from the capillary opening of a funnel gage of a fine spray, even when the capillary tube is tightly encased in rubber.

tion pressure of sound and the amount of energy necessary to convert a gram of substance from infinite radius to a small finite radius are both easy to estimate, but no specific mechanism can be formulated for the emulsification process and without this the two cannot be usefully equated. Since, moreover, the standing waves in liquids are shifting constantly both in intensity and in position, it seems certain that, even if it occurred, emulsification would under these conditions lead to no useful conclusions.

Summary

It has been demonstrated that emulsions produced by sound waves are due largely to action at the walls of the vessel. A method has been devised whereby the process of emulsification may be used as a fairly reliable measure of relative intensities of sound. An argument is advanced which makes it appear unlikely that absolute radiation pressures can be calculated from any similar process. It has been demonstrated that the walls of a glass vessel are slightly emulsified and that small uniform glass particles in liquids are not fractured by intense sound waves.

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A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. III. THE ANALYSIS OF NICKELOUS BROMIDE

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In two recent investigations comparisons of terrestrial and meteoric nickel have been made by the quantitative determination of nickel in nickelous oxide[1] and of chlorine in nickelous chloride.[2] In both series of experiments the meteoric nickel was obtained from the same source, the Cumpas meteorite found in 1903, near Cumpas, Sonora, Mexico. In neither case could any difference be detected between the atomic weights of terrestrial and meteoric nickel larger than the error of the experiments. Since the origin of any meteorite must necessarily be largely a matter of conjecture, the possibility of a difference in the isotopic composition of nickel from different meteorites, although remote, is not negligible. Therefore, the availability of a considerable quantity of meteoric nickel from another source has led us to a new comparison of this material with that of terrestrial origin. In order to vary the method somewhat from those outlined above and in order to take advantage of the very great suitability of silver bromide for precision work, in this case nickelous

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[1] Baxter and Parsons, THIS JOURNAL, **43**, 507 (1921).

[2] Baxter and Hilton, *ibid.*, **45**, 694 (1923).