lyzed behind this filter which was compensated, at each wave length, for the photochemical efficiency of this photolysis according to (unpublished) data by P. A. Leighton. Changes in total intensity and in spectral energy distribution are integrated by this device. The losses per hour in iodine value y were for seven carbon arcs, cored and uncored, plotted as ordinates against x, the reciprocals of times in which the same sources, without filters, produced a standard erythema. Roughly, $y = ax$. For the more efficient sources, $y = ax + b$ is preferable. The indicated threshold value will be further studied. Similar chemical actinometers for such purposes as photography, antirachitic therapy or even chlorophyll assimilation are possible.

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[A CONTRIBUTION FROM THE ALFRED LOOMIS LABORATORY OF TUXEDO, NEW YORK, AND THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE CHEMICAL EFFECTS OF HIGH FREQUENCY SOUND WAVES
I. A PRELIMINARY SURVEY

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Introduction

Experiments on the production of sound waves for submarine signaling by a reversal of the Curie piezo-electric effect with quartz crystals in oscillating fields have been in progress for some time in several countries.[1] Since, however, the kinematic coefficient of viscosity increases as the square of the frequency, high frequencies would be absorbed rapidly in water, and these experiments have necessarily been conducted at relatively low frequencies. Recently one of us in conjunction with R. W. Wood[2] has shown that sound waves of great intensity may be similarly produced in high frequency fields, and that they are readily absorbed by liquids and solids. For this purpose a 2-kilowatt oscillator, capable of producing powerful oscillations with frequencies from 100,000 to 500,000 per second was employed; the quartz crystals, varying from 6 to 12 mm. in thickness and 50 to 80 mm. in diameter, were immersed in oil between two electrodes. The voltages used in submarine signaling are of the order of 1500, but the limiting voltage in our work is determined only by the sparking distance in oil between the two electrodes. In this way voltages of the order of 50,000 are possible and a corresponding increase in intensity of radiation is secured, since the amplitude of vibration

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[1] A review of the literature on this subject is given in I. B. Krandall, "Theory of Vibrating Systems and Sound," McGraw-Hill Book Co., N. Y., **1926**, p. 142.

[2] Wood and Loomis, *Phil. Mag.*, vii, **4**, 417 (1927). This paper contains a comprehensive account of the physical and biological effects of supersonic waves, including detailed description of the apparatus for producing them.

of a quartz crystal increases directly with the voltage applied to it. The intense sound waves travel up through the oil into any vessel suspended in it.

Although no investigations on the chemical effects of compressional waves so produced have come to our attention, it is apparent that two correlated types of phenomena may be expected, and it is the purpose of this investigation to demonstrate their existence and order of magnitude. In the first place a series of standing waves set up by these vibrations consists of nodes and loops, matter in the nodes being relatively quiescent and in the loops being under varying tension. Therefore, at points of rarefaction in the standing waves, cavitation and similar phenomena involving the formation of a vapor phase are to be expected. Secondly, in the compressed regions of the standing waves an increase in kinetic energy density occurs, which corresponds to a local increase in temperature. Since the average temperature of the system is unaltered by this, the sound waves should have only an impalpable effect on the equilibrium constant of any chemical reaction. Such temperature changes should, however, affect the rate of a reaction, where temperature plays a considerable part, in so far as its temperature coefficient deviates from linearity, and a velocity constant corresponding to a higher temperature than that measured with a thermometer should be obtained. In the ordinary nearly balanced reaction, say the esterification of ethyl alcohol by acetic acid, it is possible that the increase in temperature of the condensed portion of the wave, and its corresponding increase in reaction velocity, would be so nearly balanced by the decrease in temperature in the rarefied portion that the measurable result on the reaction velocity would be negligible. On the other hand, in reactions which proceed irreversibly, or in any reaction extremely far from its equilibrium point, the gain in velocity of the condensed portion should not be offset by the loss in the rarefied portion, and the effect should be shown indisputably. It was a tentative argument of this kind which led to the experiments described below.

A third possible effect should be mentioned, although it cannot be treated in detail in this communication, namely, the effect of the vibration frequency of the sound wave itself on an unstable molecule, apart from its local kinetic effect upon molecules collectively. Although the frequencies used in the work described below (289,000 per second unless otherwise stated) were of a magnitude far below that of molecular vibration, certain effects, to be discussed later, seem to substantiate such an hypothesis.

General Effects

Many sensitive metastable systems are discharged by the sound waves in accordance with the foregoing discussion. Nitrogen tri-iodide is, for example, exploded when subjected to sufficiently intense radiation;

this cannot be produced by touching a watch glass containing the dried explosive to the radiated oil, but occurs only when the iodide, moist, is plastered on an "accumulator" of radiation—a fine filament drawn from the neck of an Erlenmeyer flask, the bottom of which is suspended in the radiated oil. Under these conditions the iodide collects in beads in standing waves in the glass filament, and is exploded progressively from the top to the bottom of the filament as it dries. Less sensitive explosives like ammonium nitrate, however, remain unaffected. Yellow mercuric iodide is converted to red below 120° by the sound waves, but the contact between the dry iodide and the glass is poor, and regular sound-patterns cannot be so produced. No other allotropic changes of those investigated (for example, sulfur, phosphorus, etc.) were sufficiently sensitive to give consistent results.

The sound waves have an explosively discharging effect on superheated liquids; carbon tetrachloride, for example, superheated 5° evaporates so violently as to half empty the test-tube which contains it. Similarly, carbon dioxide supersaturated in water is violently relieved, but without the spectacular consequences attendant upon the relief of superheating. Supersaturated solutions of crystalline solids in liquids and supercooled liquids are, on the other hand, little affected. A sirupy solution of sodium thiosulfate was discharged by radiation collected by an "accumulator," a metastable crystal modification being produced. A sugar "glass," liquid salol supercooled 30°, and similar solutions and liquids gave, however, no consistent results. This is easily understood when it is remembered that the effect favoring the relief of supersaturation is in this case only that corresponding to the increased probability of germ formation due to the rise in temperature in the compressional waves.

The effect of the radiation on the critical phenomena in ether was investigated in the hope that banded regions of opalescence would be produced just above and just below the critical point. A great difference in appearance rayed and unrayed was observed, the time of opalescence extending over a much greater period in the latter. During the instant when the critical point was being approached from above, mottled patterns of opalescence were unquestionably observed in the rayed tubes, but either the phenomenon was not sufficiently marked, or the interference pattern of the glass was too complex, to permit its assignation to standing waves. Cinematographic records have been made, and it is hoped that they will reveal greater regularity than the eye can perceive.

One further effect of a chemical nature is sufficiently marked to warrant special mention: namely, the "atomization" of a substance at a liquid or gaseous interface. In this way emulsions of metallic mercury in water were produced which reduce potassium permanganate and remain in suspension for several days. Similarly a test-tube of distilled water clear to the Tyndall beam before raying, becomes faintly turbid after raying, due to small glass fragments which are "atomized" from the walls. Because of this the rays are of no value whatever for the coagulation of microscopic particles, even fairly coarse suspensions such as silver chloride precipitated in water remaining unflocculated on raying.

Certain more physical effects of the rays are also important from the point of view of the experiments detailed below. When a test-tube of liquid is suspended over the oil-bath in which the crystal is oscillating, the sound waves which rise through the oil pass through the walls of the test-tube into the liquid and are absorbed, heating it rapidly. They also set up standing waves in the glass which, by friction with the liquid, produce heat. Such heating changes the average or integral temperature by sound radiation, and must be carefully distinguished from the local temperature effects discussed above. This general heating affects the liquid as long as sound waves reach it; jacketing with ice and water diminishes the intensity of radiation which reaches a vessel but in no way diminishes the heating of the liquid by that portion which enters it. Any other thermostating device would be equally futile and, isothermal conditions being impossible, quantitative measurements in the sound waves can be made only by following the rise in temperature. Here, however, another peculiarity of the radiation intervenes. The compressional waves enter the mercury of an ordinary thermometer, setting up standing waves in the walls of the bulb, and causing it to read many degrees higher than the actual temperature in the liquid. Again, heat produced at the liquid-glass interface causes a rise in temperature greater than that in the surrounding liquid, which further invalidates any readings made during the progress of raying. A thermocouple is equally if not more ineffective for measuring temperature during raying, since heat is generated at the metal-liquid interface which causes a high local temperature (dependent largely on the viscosity of the liquid), and a lag in determining the true temperature after discontinuing the radiation which is greater even than that of a mercury thermometer. Thus a singular difficulty is encountered in quantitative work; it is impossible to work isothermally, yet no adequate measure of the temperature during radiation has been found. The methods of extrapolation and interpolation used below are not extremely satisfactory, but at least give the temperature at any instant within 0.1°.

Furthermore, when a vessel is immersed in the radiating oil-bath, its distance above the quartz crystal is of immense importance for the obtaining of reproducible results; when this distance is made an exact number of half wave lengths, standing waves are produced between the crystal and the bottom of the vessel which greatly increase the intensity of effect in the vessel. This is clearly illustrated by the following results, obtained with a flat-bottomed beaker 5 cm. in diameter containing 50 cc. of water, which was lowered beneath the surface of the oil by a micrometer screw, being rayed at successive points in its descent.

TABLE I

THE RESONANCE EFFECT ON THE HEATING OF WATER

Distance from surface of oil in cm..................	0.	0.164	0.218	0.246	0.310	0.385	0.447	0.492	0.556
Rise in temperature for 30 seconds raying.........	2.7	2.2	0.85	1.5	2.2	2.0	0.8	0.6	1.5

This series of observations gives a value for the velocity of sound in oil at a frequency of 281,000 per second of 1420 meters per second, probably the only determination at anything like this frequency which was in existence at the time it was made. Recently J. C. Hubbard and one of us[3] have utilized a similar principle to measure very exactly the velocity of sound in liquids.

Since, therefore, the amount of heating in the liquid is not exactly determinable, and since it is affected by the frequency of the oscillating circuit which is changed by the temperature of the quartz crystal, by the heating of the oil, by the height and configuration of the vessel, and even perhaps by the pressure hysteresis of the vessel, the reproduction of quantitative results by magnitude rather than by percentage error has alone been attempted in the sections which follow. A large test-tube with a hemispherical bottom has been found to minimize many of the sources of error outlined above, since it bridges several half wave lengths, and hence is almost devoid of tuning effects, but loses of course, in consequence, some of the energy of the waves by interference. It has been used wherever possible below.

The Lowered "Boiling" Temperature of Liquids

Preliminary measurements showed that, besides relieving superheated liquids, the sound waves would produce bubbles of vapor in air-free liquids at about 1° below their boiling temperature. Results of this kind were obtained with water, toluene, carbon tetrachloride and ether. It became, therefore, of interest to investigate the magnitude of this effect and its variation with the intensity of radiation.

Water and carbon tetrachloride were selected because of their ease of purification, chemical and associative dissimilarity and non-inflammability. A number of devices to secure slow cooling from the boiling point of these liquids were tried, the most satisfactory being jacketing the tube under observation with a spaced cage of German silver wire through which a voluntarily variable current was passed. In this way temperatures in the neighborhood of the boiling point of the liquid could be maintained to ±0.05° for several minutes. These were read by a thermometer held in the tube with a cork, through which passed also a ring stirrer to insure even heating throughout the liquid.

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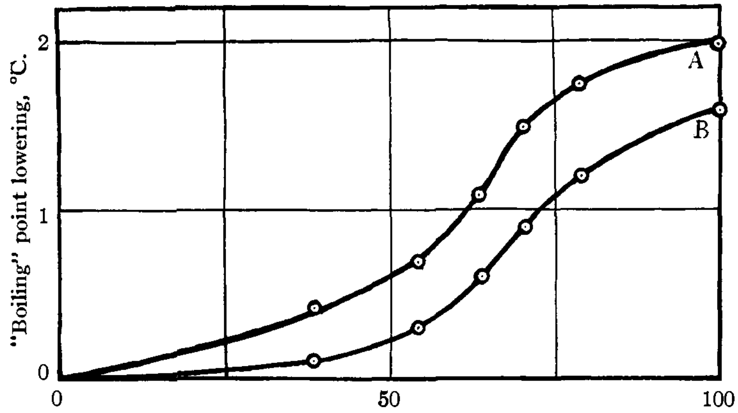
[3] Hubbard and Loomis, *Nature*, **120**, 189 (1927).

At a given temperature, the stirrer was clamped above the surface of the liquid to prevent local frictional heating, and the tube was lowered into the oil while the latter was being radiated with a predetermined intensity. The liquid had of course been scrupulously freed from dissolved gases by boiling. If bubbles of vapor at once appeared in the center of the tube, which was illuminated by a powerful beam of light to facilitate observation, the liquid was considered to "boil." If bubbles appeared only after five seconds it was considered not to "boil." The temperature was then readjusted and the observation repeated. Ten trials fixed the lowest temperature for which water would "boil" with a given intensity of radiation within ±0.05°, with carbon tetrachloride within ±0.10°. The intensities of radiation were determined by the heating effect of thirty seconds of radiation upon 25 cc. of water in a test-tube at 25°, the voltage in the oscillating circuit being altered at will. A relative intensity of 100% heated 25 cc. of water 2.8°, and 25 cc. of carbon tetrachloride 5.2° in thirty seconds.



Intensity of radiation, %.

A, carbon tetrachloride; B, water.

Fig. 1.—The lowering of the "boiling" point of water and carbon tetrachloride at atmospheric pressure by high-frequency sound waves as a function of the relative intensity of the radiation.

The results of this series of measurements are given below and are plotted in Fig. 1.

TABLE II

THE EBULLITION OF AIR-FREE WATER WITH VARIOUS RADIATION INTENSITIES AT ATMOSPHERIC PRESSURE

Relative intensity, %	100	79	70	63	54	46	40	0
"Boiling" point of water	97.8	98.2	98.5	98.8	99.1	99.2	99.3	99.4
"Boiling" point of CCl_4	75.1	75.3	75.6	76.0	76.4	76.7	..	77.1

The actual boiling point at atmospheric pressure (0% intensity) was determined in the vapor of the liquid in a distilling flask, the barometric pressure being for the water determinations 744.8 mm. and for the carbon tetrachloride 743.5 mm.

In the hope of facilitating the interpretation of these results, measurements were also made in a very similar apparatus with air-free water and carbon tetrachloride hermetically sealed under their own vapor pressures. The results for carbon tetrachloride were not reproducible, a lowering in the ebullition point of about 15° being observed for 100% intensity. Those for water were reproducible to ±1.0°, but are not very satisfactory for the interpretation of the phenomenon since the exact point at which, under these conditions, water ceases to boil under its own vapor pressure is not clear.

TABLE III

THE EBULLITION OF AIR-FREE WATER UNDER ITS OWN VAPOR PRESSURE

Relative intensity, %	100	79	70	63
Temperature of ebullition	51.0	53.5	57.0	61.0

With lower intensities the results were scattered, an intensity of 30% producing no ebullition at 85°, a temperature far above 63° where ebullition could still be produced by jarring the tube without supersonic waves.

The interpretation of these results is difficult and can be attempted only tentatively. The falling off of the effect on the ebullition point with increasing intensity above 70% means, owing to its method of measurement, only that the heating effect of the waves increases more than their vapor-forming effect. That the function is of the same type in both cases plotted in Fig. 1 suggests that with increasing intensities complex interference patterns are set up in the vessel employed, and more of the radiation heats the liquid from contact with the walls, while less enters it to effect vaporization per unit rise in temperature of the system. This agrees with the qualitative observation that sound patterns on glass plates are best developed with low radiation intensities. The "boiling" point lowering of carbon tetrachloride is less than its greater heating effect per cubic centimeter would lead us to expect at high intensities, for carbon tetrachloride is raised in temperature 1.8 times as much as water, and $1.8 \times 1.6° = 2.9°$, whereas the "boiling" point lowering in carbon tetrachloride at 100% intensity is only 2.0°.

In attempting to discuss the significance of the results it must clearly be borne in mind that, as has been already indicated, sound waves hardly can produce a general effect on physical equilibria in such a system as water-water vapor, and hence that all explanations must be referred to local variations in the properties of the liquid in standing waves. Unfortunately the vapor pressure changes corresponding to different intensities in the three cases quoted above have no uniformity, and the fundamental mechanism of the local phenomenon must be left undetermined. Arguments of about equal weight may be advanced that this "boiling" takes place in the compressional or in the rarefied portion of the wave. In the former the temperature is higher and the pressure more intense; these changes tend to produce boiling in the liquid since both raise its vapor pressure.

Also, at a higher temperature, the surface tension of the liquid is diminished, making it easier to form a bubble of vapor which is not redissolved; this effect is probably negligible at atmospheric pressure, but seems to become very important when the liquid "boils" under its own vapor pressure. On the other hand, in the rarefied portion of the wave the liquid is under tension, which would tend to produce cavitation and the formation of vapor at less than atmospheric pressure. In this region, however, the temperature is lower, the surface tension higher, and the tendency of the vapor to form therefore diminished. No data are at hand to decide which of these two effects produces the result and we must be content with the statement that they cannot reinforce each other. If the former is effective, the artificial "boiling" may be said to be equivalent to actual local boiling, since the vapor is liberated at something more than atmospheric pressure; if the latter, the "boiling" must be considered merely a low-pressure ebullition. The sole observation which enables a choice to be made is that the bubbles rise, slowly diminishing in size to the surface through 5 cm. of liquid, and are hence probably at not less than atmospheric pressure, but this can by no means be considered conclusive evidence.

The Expulsion of Gases Dissolved in Water

A flask of water at 25° which has previously been saturated with air at 30° and then tightly stoppered becomes, upon being radiated, at once filled with bubbles of gas released by the sound waves. Similar results are obtained when the air-saturated liquid is carbon tetrachloride, methyl or ethyl alcohol, benzene, etc. Measurements were made to demonstrate the reality of this effect and the conditions which govern it.

The vessel in which the gases were liberated was constructed from a 200cc. Pyrex Erlenmeyer flask. A vertical side tube, goose-necked, and containing a small capillary constriction, was attached to this about half-way down its side, and a ring seal blown in the neck which projected a small bore test-tube almost to the bottom of the flask. This ring seal was sloped so that any gas caught under it would collect at a single point and at this point was sealed a stopcock. The volume of the flask was then measured from the under side of the barrel of the tap to the beginning of the capillary constriction. In filling the vessel with liquid to be rayed it was first dried and brought to the temperature of the thermostat, and the air which it contained swept out by the saturating gas under observation. It was then filled from a reservoir of gas-saturated liquid at the same temperature and, all bubbles of gas having been excluded, was rayed until its temperature, measured with a tested accuracy of 0.03° by a thermometer immersed in a little water in the test-tube set in the neck, had risen an appropriate amount. The gas liberated collected below the tap and was ejected into a gas buret of the usual type which gave its volume to 0.01 cc. Knowing the solubility-temperature function of the gas in the liquid under ordinary conditions, the saturation temperature and pressure, the final temperature after raying, the conditions under which the volume of the gas had been measured, and the volume of the flask, it was easy to calculate the amount ejected by supersonic rays in excess of that corresponding to the decreased solubility of the gas due to the temperature rise. The only serious experimental difficulty in the procedure was that the sound waves occasionally produced vibrations in the flask which shattered it.

The saturating gases were nitrogen and oxygen, used from "air refined" tanks without especial purification. The water was saturated by bubbling at atmospheric pressure minus the pressure of aqueous tension at 30.2° in a large thermostat. It was demonstrated chemically that three hours' bubbling was necessary to free previously air-saturated water from all but 0.5% of its oxygen by nitrogen bubbling, hence the liquid was not considered suitable for use until at least this time had elapsed during the bubbling process.

The results obtained are given in Table IV.

TABLE IV

THE EFFECT OF RADIATION ON GASES DISSOLVED IN WATER

Oxygen saturated at 30.2°, 744 mm. barometric pressure

	Determination number	1	2	3
I	Volume of vessel, cc.	201	201	201
II	Temperature after raying, °C.	39.3	37.0	34.5
III	Cc. of gas evolved (N. T. P.)	1.52	1.45	1.24
IV[a]	Cc. of gas corresponding to solubility	0.65	0.51	0.30
V	Expelling factor of rays (III/IV)	2.3	2.8	3.7

Nitrogen saturated at 30.2°, 743 mm. barometric pressure

	Determination number	4	5	6	7	8	9
I	Volume of vessel, cc.	200	200	200	201	240	242
II	Temperature after raying, °C.	38.6	36.8	39.3	36.6	36.6	36.6
III	Cc. of gas evolved	0.93	0.71	0.94	0.71	0.84	0.85
IV[a]	Cc. of gas, theoretical	.33	.27	.33	.26	.31	.31
V	Expelling factor (III/IV).	2.8	2.6	2.8	2.7	2.7	2.7

[a] The figures given after IV were obtained from the generally accepted results of Winkler for the solubilities of nitrogen and oxygen in water, and represent the difference between the volume of gas dissolved in the volume of water in question at the lower and at the higher temperature. V therefore represents the ratio between the volume of gas obtained and that calculated on the assumption that the sound waves would have no other effect than perfectly to relieve supersaturation resulting from the rise in temperature.

Each flask of different volume in the nitrogen determinations differed in type and weight. All determinations were made at 100% intensity except No. 9, which was at 70%. The constancy of the "expelling factor" for nitrogen indicates that the gas is uniformly given off throughout the period of raying and that the size and shape of the vessel and the intensity of the radiation do not affect the phenomenon; the effect of these variables has, however, been tested only over a limited range. The variations in this factor for oxygen are due to other causes.

Similar observations with carbon dioxide in water gave positive but quantitatively unsatisfactory results owing to the great solubility of the gas. With air in water the results consistently presented an interesting anomaly which will not be considered in this communication.

These measurements may be more easily interpreted than those discussed in the foregoing section, since small variations in the properties of the solvent should not, in this case, influence the result. The phenomenon may, therefore, be considered one of cavitation in the tensional regions of the standing waves, a pressure lower than atmospheric being produced locally which causes the dissolution of the gas. Therefore, it cannot be considered that the solubility of the gas is diminished in the thermodynamic sense, but only that in certain regions in the liquid conditions deviating from the average ("equilibrium") conditions are produced which cause the expulsion of gas bubbles which, rising through the liquid, are not considerably redissolved.

The Acceleration of Chemical Reactions

The purpose of this section is to demonstrate that certain chemical reactions when radiated by sound waves proceed more rapidly than is to be inferred from a strict consideration of their thermometric or integral temperature. The reactions studied must evidently be homogeneous liquid reactions since gases conduct the waves very little at ordinary pressures and solids, especially powders, are unreliable conductors. Electrometric measurements being difficult because of the exceedingly high voltages in the immediate neighborhood of the reaction under observation, the field for preliminary investigation is further narrowed to time reactions with a visual end-point, that is, "clock" reactions. A conclusively positive effect was obtained with two of the three of these which were studied.

The first, the induction period of the reduction of potassium permanganate by oxalic acid was unsatisfactory. The end-point, when the reaction was adjusted to be slow enough to allow radiation for one minute, was indefinite. Any effect of the radiation was therefore within the limit of error of observation.

The second reaction employed a familiar principle in a manner which had not come to our attention; it will later be described in detail by one of us. Dimethyl sulfate was hydrolyzed in basic solution in the presence of an indicator, in this case "brom-thymol blue." The solution contained only enough base to neutralize a quarter of the sulfuric acid liberated by hydrolysis and consequently, when neutralization had taken place, a sharp change in hydrogen-ion concentration (roughly from *P*H 8 to *P*H 3) occurred in a very few seconds, and the indicator was almost instantaneously changed in color. This reaction is especially satisfactory for the work in hand because it is easily adjustable to a wide range of reaction times, because it is not affected by oxygen in the air, and because the gradual inevitable heating due to sound waves caused the end-point only to become more sharp. The most satisfactory concentrations of constituents were obtained by adding 2 cc. of dimethyl sulfate to 100 cc. of 0.01 *N* sodium hydroxide strongly colored with neutral "brom-thymol blue." Under these conditions the end-point of the reaction was reached in 335 seconds at 23.0°, 155 seconds at 30.2° and 82 seconds at 35.3°, the end-point of a single determination being clear ±3 seconds at the lower temperature and ±1 second at the higher.

In order to determine the effect of raying, the reaction was begun in a flask and as quickly as possible transferred to two scrupulously cleaned test-tubes, one of these being subjected to radiation at zero time. The other, used as a control, was simultaneously dipped into a bath of water at about 50° and held there, vigorously stirred, for a measured length of time just sufficient to bring its temperature above that of the rayed sample after 15 seconds' radiation. After radiation had been discontinued, the next 15 seconds were occupied in ascertaining the temperature of both portions of the solution with compared thermometers. Raying was then resumed for 15 seconds with one sample while the control was again warmed to follow the new rise in temperature. The process was continued until the blue color of the indicator became suddenly yellow in both, when the total time for each was recorded. By practice it became possible to follow with the control the temperature of the rayed sample within a few tenths of a degree, keeping the former always slightly higher in temperature to make temperature errors adverse to the effect desired.

A complete temperature-time picture of two parallel rayed and unrayed samples is given graphically by curve A, Fig. 2. This represents Determination 2, Table V; by a study of this chart the method of reporting the reactions will become sufficiently clear.

TABLE V

THE EFFECT OF SOUND WAVES ON THE HYDROLYSIS OF DIMETHYL SULFATE

Determination 1. Starting temperature, 20.4°

Temperature rayed, °C	24.7	26.9	28.6	30.8	32.6	34.4	36.2
Temperature unrayed, °C	23.8	26.1	28.5	31.0	33.2	35.0	36.2
Immersion of unrayed, seconds	4	11	12	14	16	14	15

Reaction time rayed, uncorrected, 195 seconds; corrected to 30.0°, 177 seconds.
Reaction time unrayed, uncorrected, 195 seconds; corrected to 30.0°, 178 seconds.

Determination 2. Starting temperature, 22.5°

Temperature rayed, °C	22.9	24.9	27.0	29.0	30.8	32.4	34.0
Temperature unrayed, °C	23.2	25.4	27.8	30.2	31.4	32.4	34.0
Immersion of unrayed, seconds	3	5	8	7	4	6	13

Reaction time rayed, uncorrected, 195 seconds; corrected to 30.0°, 204 seconds.
Reaction time unrayed, uncorrected, 193 seconds; corrected to 30.0°, 218 seconds.

Only two determinations are reported since they represent the most conclusive and the most inconclusive results obtained, and the space which they require is disproportionate to their importance. In Determination 1 the effect of raying is within the limit of error of observation and the result must be considered doubtful. In the other an acceleration by raying has been obtained, as is made clear by the corrected reaction time value at 30.0°. This was obtained by use of the temperature coefficient, the data for which are given above, on the assumption that it is independent of concentration over a small range, and by use of the approximation that over 2° intervals the temperature-reaction-time function is linear. Because both these simplifications are entirely reasonable, and because, moreover, any errors introduced by them affect equally the control and the rayed portion of the solution, it is estimated that the reaction times corrected to 30.0° are accurate to better than 1%. The acceleration of the reaction, averaged from all results, was 10 seconds at 30.0°.

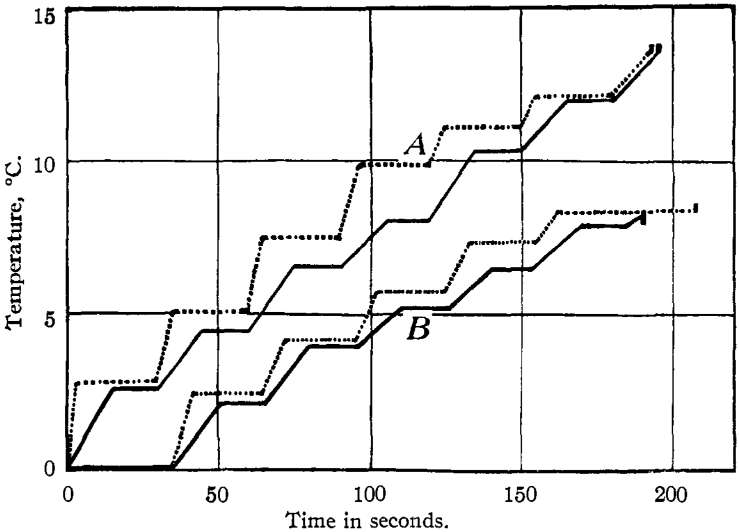


Fig. 2.—A temperature-time picture of two reactions accelerated by sound waves. *A* represents the hydrolysis of dimethyl sulfate, *B* the iodine "clock" reaction; in each case the temperature of the unrayed control solution is indicated by a dotted line. The starting temperature of *A* was 20.4°, of *B* 23.8°.

It is perhaps disappointing that no more conclusive uniformity in the accelerating effect of the sound waves is here observed. To account for the divergence of the results it is only necessary, however, to recall the great difficulties encountered in reproducing the experimental conditions in any two parallel determinations.

The third reaction observed was the long familiar iodine "clock" depending upon the reduction of potassium iodate by sulfurous acid. This gave a much more clearly positive, although more difficultly interpretable, result. Solutions 0.01 M to KIO_3 and 0.0164 M to Na_2SO_3 were prepared, the latter being made 4.6×10^{-4} N in sulfuric acid and containing also a suitable quantity of boiled starch. At a given instant 25 cc. of iodate solution was mixed with 55 cc. of sulfite solution, both at a measured temperature, and thoroughly shaken. After mixing the solution was at once poured into two large scrupulously clean test-tubes, and one of them subjected to 15 seconds' radiation while the other was externally warmed. The tubes were subsequently treated exactly as in the study of the previous reaction. The results obtained are reported in Table VI.

TABLE VI

THE EFFECT OF SOUND WAVES ON THE IODINE "CLOCK" REACTION

Detn. no.	Rel. intens., %	Time elapsed before raying, seconds	Temp. at start, °C.	Average temp. during raying, °C.	Final temp., °C.	Time end-point reached, seconds
1a	100	45	23.5	26.8	29.5	190
1b	0			29.0	34.0	210
2a	100	55	25.0	27.7	30.1	190
2b	0			28.7	31.4	205
3a	100	45	24.0	28.2	32.1	190
3b	0			29.6	33.5	210
4a	100	55	25.0	28.2	31.2	188
4b	0			28.9	33.3	207
5a	100	40	25.0	29.1	33.0	188
5b	0			30.0	34.1	203
6a	70	45	25.0	27.7	29.9	180
6b	0			28.6	31.0	206
7a	70	40	24.5	27.1	29.4	183
7b	0			27.7	30.0	208
8a	54	40	25.0	26.8	28.4	190
8b	0			27.8	28.6	215
9a	0	30	24.5	..	25.2	222
9b	0			..	25.5	224
10a	40	30	23.8	25.6	27.1	204
10b	0			26.3	27.5	227
11a	100	34	23.8	28.1	32.1	190
11b	0			28.5	32.1	207
12a	57[a]	41	24.5	26.5	28.6	192
12b	0			26.9	28.9	214

[a] This determination was carried out at a frequency of 324,000 per second, all others being at 289,000 per second.

In this table the *a* determinations have been subjected to radiation and the *b* determinations heated to follow their rise in temperature. A temperature-time picture of Determination 11 is presented graphically in Curve B, Fig. 2; here the time that elapsed before radiation was begun has also been plotted to give a complete picture of the reaction. Determination 10 was subjected to six 15-second periods of raying, and the other determinations each to five 15-second periods. The measurements included in Table VI are representative of over thirty similar observations made. In no case were anomalous results observed which are not represented in the table. Number 9 of these determinations is a very important check upon the general conditions of the reaction; it was carried out exactly as the others except that the tube containing the radiated sample barely touched the radiated oil, and the intensity of sound waves entering it was therefore negligible, the slight heating effect observed being due only to the fact that the oil temperature was about 30°. This determination eliminates at once the possibility that the reaction is accelerated by the high frequency field.

It is unnecessary to apply a correction for the difference in temperature between the rayed and unrayed solutions in these measurements, and hence individual heating curves have been averaged during the period of raying. The temperature coefficient of this reaction is abnormal, varying considerably with the concentrations of the components. The reaction times of these solutions were 244 seconds at 20.7°, 188 seconds at 30.2° and 174 seconds at 33.1°. Since this function is nearly linear and its slope very abnormally low, the small difference in temperature between the two solutions affects their reaction times only by a factor of the second order. Since each control is at all times kept slightly above the temperature of the corresponding rayed solution, acceleration of the latter due to temperature errors is impossible, and the results are most clearly reported as they were actually observed.

Several aspects of this reaction, in contradistinction to that preceding it, strongly suggest that a factor much more powerful than the mere deviation of its temperature coefficient from linearity is involved. In the first place, the temperature coefficient of the reaction is abnormally low, a change from 25° to 35° decreasing the time by only about 25%. Furthermore, the lack of variation of the accelerating effect with intensity of radiation is exceedingly puzzling if the higher temperature of the condensed region alone is the activating agent. Finally, the excessively large effect upon the reaction velocity in comparison with that of the hydrolysis of dimethyl sulfate, and its far greater reproducibility, at once suggest a difference in action in the two cases. As a tentative explanation for these phenomena it does not seem unreasonable to suppose that the frequency of the sound waves themselves had a disintegrating effect upon some compound found in the complex chain of reactions which led to the ultimate liberation of iodine. In order to test this hypothesis Reaction 12 was carried out at a higher frequency, no quartz crystal of lower being readily available. The results show that if frequency of vibration is a determining factor it is a "band" rather than a "line" effect, but this does not in the least invalidate the hypothesis. A systematic potentiometric investigation into the stability of the various compounds involved in this reaction and of other unstable molecules under sound radiation of various frequencies will at once be undertaken. In this field, as well as in several others which we can only suggest in so cursory a survey of the chemical phenomena produced by high frequency sound waves, we hope to obtain further information in the near future.

Summary

It has been demonstrated that intense high frequency compressional waves produce certain chemical effects, especially discharging metastable systems of great sensibility. They furthermore expel gases from liquids, cause ebullition in pure liquids at temperatures considerably below their boiling points at atmospheric pressure, and accelerate certain chemical reactions. The conditions of intensity and frequency affecting these phenomena have been considered. The reasons for this action are discussed, tentative explanations for various anomalous effects being advanced.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. VI. THE PHOTOCHEMICAL REACTION BETWEEN OXYGEN AND MERCURY VAPOR AT RELATIVELY LOW PRESSURES

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The fundamental researches of Cario and Franck,[1] which showed that active hydrogen is produced by the illumination of a mixture of hydrogen and mercury vapor with the resonance radiation of mercury, have led to many interesting results in photochemical work. Nearly all of the reactions studied have involved hydrogen or molecules containing hydrogen atoms.

Dickinson and Sherrill[2] have shown that ozone is formed when a mixture of oxygen and mercury vapor is exposed to the resonance radiation of mercury in a dynamic system. They also observed the formation of a brown deposit which they assumed to be mercuric oxide. It is difficult to make determinations of the quantum efficiencies of reactions involving the resonance radiation of mercury due to the exceedingly small width of the absorption line of mercury vapor at 253.7mμ, but Dickinson and Sherrill showed that at least seven molecules of ozone were produced per mercury atom passing through the reaction vessel.

The present work was started with the object of ascertaining whether

[1] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

[2] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).