

0.03 to 0.15%. This is the range occurring in the majority of human urines. These concentrations sensitize the Benedict test for the very concentration range of glucose (0.05–0.3%) which yields doubtful results by other methods. A higher creatinine content, such as 0.2%, fortunately not common, in a urine containing 0.1% of glucose, delays the appearance of the opacity beyond the three-minute water-bath time recommended,²² while the 0.4% creatinine level reported by Folin²⁴ for a starch and cream diet prevents the precipitation entirely, as it would in any other copper reduction test. On the other hand, creatinine concentrations below the optimum range, which can occur readily after copious water intake, cause the urine to react like an aqueous glucose, so that a 0.1–0.3% glycosuric urine with less than 0.03% creatinine gives in the Benedict test only a barely perceptible red haze, which would be considered negative by its author's instructions. In the Fehling or Trommer tests such a urine would give typical positive results.

It is evident, therefore, that at low glucose levels it is the accompanying content of creatinine which determines the sensitivity of a Benedict test. With this knowledge and the better under-

(22) Benedict recommended one to two minutes of boiling over a flame. A three-minute period in a water-bath was shown by Folin and McEllroy (ref. 23) to be equivalent to the two minutes over a flame. The five-minute water-bath time, recommended in many texts, is an unwarranted extension and leads to many doubtful or false positive tests.

(23) Folin and McEllroy, *J. Biol. Chem.*, **33**, 513 (1918).

(24) Folin, *Am. J. Physiol.*, **13**, 66 (1905).

standing of the role of the various ingredients of alkaline copper solutions which has accumulated in the years since the appearance of Benedict's method, it may be possible to devise a more nearly infallible test and one sensitive to any significant concentration of glucose in urine. Progress of work on improved methods for the detection of sugar in urine is to be reported in a later paper.

Summary

1. Benedict's test, in distinction to other alkaline copper tests used for the qualitative detection of sugar, is more sensitive to urinary glucose solutions than to aqueous ones.

2. Creatinine is the opacity promoting or sensitizing factor in urine which causes bulky opacity in positive Benedict tests with low concentrations of glucose.

3. The properties of cuprous creatinine account for the interfering effect of creatinine in the precipitation of cuprous oxide in Trommer's and Fehling's tests, and for its opacity promoting effect in the Benedict test.

4. The concentration of creatinine present in the majority of human urine samples has opacity promoting properties in the Benedict test on low glucose urines.

5. Exceptional concentrations of creatinine, higher or lower than the normal proportions, may lead to false results in the Benedict test.

1619 SPRUCE ST., PHILADELPHIA, PA.

RECEIVED NOVEMBER 1, 1938

[CONTRIBUTION FROM THE PHYSIOLOGICAL LABORATORY, PRINCETON UNIVERSITY]

Sonoluminescence and Sonic Chemiluminescence

BY E. NEWTON HARVEY

Introduction

It is customary to designate a luminescence by the method of excitation, as electroluminescence, photoluminescence, triboluminescence, etc. Accordingly the luminescence which appears when sound waves pass through liquids has been called acoustic or sonic luminescence, for short, sonoluminescence. This type of light emission was first observed by Frenzel and Schultes¹ for supersonic and by Chambers² for audible frequencies. Using a magnetostriction oscillator of 8900 frequency, Chambers studied 36 pure liquids and

(1) Frenzel and Schultes, *Z. physik. Chem.*, **27**, 421–424 (1934).

(2) Chambers, *J. Chem. Phys.*, **5**, 290–292 (1937).

found 14 of them to luminesce, the brightness varying inversely as the temperature and directly as the product of viscosity and dipole moment.

Frenzel and Schultes were led to look for luminescence accompanying supersonic waves in water from the formation of hydrogen peroxide which many observers (Schmitt, Johnson and Olson,³ Beuthe,⁴ Liu and Wu,⁵ and Flosdorf, Chambers and Malisoff⁶) have found in fluids subjected to sonic treatment. Beuthe⁴ believes

(3) Schmitt, Johnson and Olson, *THIS JOURNAL*, **51**, 370–375 (1929).

(4) Beuthe, *Z. physik. Chem.*, **163**, 161–171 (1929).

(5) Liu and Wu, *THIS JOURNAL*, **56**, 1005–1007 (1934).

(6) Flosdorf, Chambers and Malisoff, *ibid.*, **58**, 1069 (1936).

the hydrogen peroxide arises from frictional electrical discharges (Reibungselektricität) which lead to activation of oxygen in cavitated air bubbles and reaction of the oxygen with water to form hydrogen peroxide. Such discharges themselves easily could give rise to luminescence, with hydrogen peroxide formation a secondary effect.

A more extended investigation of the luminescence is described by Levsin and Kzevkin.⁷ They found that four times distilled water will luminesce and conclude that the light is due to electrical discharge in water vapor in cavities within the liquid. All observations, including my own, agree that the luminescence appears when fluids are completely shielded from the electrical field and that it is always connected with cavitation, being brightest where cavitation is most marked.

Electric potentials produced by increase in the surface of a fluid (as when it is atomized) are called balloelectric or Lenard potentials (Wasserfallelektricität) and were first suggested as an explanation of the extraordinary chemical effects of cavitation in hydraulic problems by Föttinger.⁸ They have been emphasized by Richards⁹ who, in collaboration with G. Hobart, was able to detect random variation in potentials in water in the cavitating region of a Reynolds tube.

If sonoluminescence is due to electrical discharge, it should make little difference what gas is dissolved in the fluid, provided cavitation of the gas occurs. On the other hand, if light emission depends on the activation of oxygen, *i. e.*, if it is a chemiluminescence, there should be no luminescence in hydrogen or nitrogen. Actually both types of luminescence can be observed under different conditions. Experiments to determine these points together with other observations on sonoluminescence are reported herein. The most striking effect is the sonoluminescence of bromine water which emits a light far brighter than that of water alone or of water with any other added substance.

Apparatus.—The oscillator (in a light-tight box) is of the tuned grid tuned plate type with two push-pull 852 tubes and a power input of approximately 300 watts. The quartz crystal is 5.3 cm. in diameter and 0.51 cm. thick, between two thin copper electrodes in transformer oil. Its natural period is 550 kilocycles. At full power,

(7) Levsin and Kzevkin, *C. R. Acad. Sci. U. S. S. R.*, **16**, 399–404 (1937).

(8) Föttinger, "Hydraulische Probleme," V. D. I. Verlag, Berlin, 1936, p. 14.

(9) Richards, *Rev. Modern Phys.*, **11**, 36–64 (1939).

a fountain of oil about 4 cm. high is produced, making possible a demonstration of the well known phenomena associated with supersonic waves, including cavitation of gas.^{9–14} The oscillator is not strong enough to cavitate vapor from a degassed fluid such as water. Glycerol or nitrobenzene also gave no evidence of cavitation. Black paper screens prevented an occasional sparking at electrodes from disturbing the observation of luminescence in fluids which were placed in test-tubes and touched to the surface of the oil over the crystal. Unless otherwise mentioned the temperature was about 20°.

It gives me great pleasure to thank Mr. Charles Butt, Research Assistant in Physiology, for constructing the oscillator and for faithful assistance during the experiments, and Mr. Alfred L. Loomis, Tuxedo Park, N. Y., for the loan of the quartz crystal and other apparatus.

Effect of Gases.—Pure water cavitates in the supersonic apparatus here described when saturated with air, nitrogen, hydrogen, oxygen and neon but not (or only slightly) if saturated with carbon dioxide or if evacuated with a filter pump or if saturated with air at atmospheric pressure and placed under 1.7 atm. hydrostatic pressure. However, luminescence only appears in air, oxygen, neon and weakly in nitrogen. In hydrogen purified by passing over heated platinized asbestos, there is no trace of luminescence. This might indicate that sonoluminescence depends on oxygen.

However, if nitrogen (purified by passing over freshly reduced copper in the apparatus described by Kendall¹⁵ and led to an all-glass vessel by lead tubing sealed with de Khotinsky cement) is bubbled through distilled water for one and one-half hours, a weak luminescence still appears in the water when exposed to supersonic radiation. There is not enough oxygen present in this nitrogen to allow luminescence of luminous bacteria, which can detect about 0.01 mm. oxygen.¹⁶

Since luminescences are extraordinarily sensitive tests for oxygen, another method of purifying the nitrogen was used. It was mixed with 2.5% hydrogen in one experiment and with 7% in another. The mixture was then passed over heated platinized asbestos in a quartz tube connected with the vessel by a lead tube. Water saturated with nitrogen purified in this way still showed a faint sonoluminescence in high frequency sound waves and the conclusion is reached that *oxygen is not necessary for sonoluminescence of water.*

The neon gas experiments were undertaken in the hope of observing the characteristic reddish glow from electrical excitation of neon when water saturated with neon is radiated with supersonic waves. Water in a glass test-tube sealed to a 120° stopcock was thoroughly exhausted of gas by boiling at reduced pressure, cooled to 0° and

(10) Wood and Loomis, *Phil. Mag.*, **6**, 418 (1927).

(11) Bergman, trans. by Hatfield, "Ultrasonics," Chapman and Hall, London, 1938.

(12) Dognon and Biancani, "Ultra-Sons et Biologie," Paris, 1937.

(13) Wood, "Supersonics," Brown University Press, Providence, 1939.

(14) Harvey, *Biol. Bull.*, **59**, 306–325 (1930).

(15) Kendall, *Science*, **73**, 394–397 (1931).

(16) Harvey and Morrison, *J. Gen. Physiol.*, **6**, 13–19 (1923).

saturated with neon. When the tube was touched to the supersonic fountain of oil a luminescence appeared of about the same intensity as when water saturated with air at 0° is tested. No trace of red color that might be evidence of excitation of the neon by electrical discharge appeared and no difference in intensity or shade was detected when neon saturated and air saturated sonoluminescence was observed through red, orange or blue-green filters. The neon in the tube gave a bright red luminescence when excited with a leak tester at 0° but none at 20°, due to quenching by water vapor.

Either sonoluminescence in neon (1) is too weak to distinguish color or (2) excitation of the neon does not occur within the cavitated gas bubbles. That the first explanation is correct can be proved easily by a direct experiment. The light from a neon lamp at different distances falling on an opal glass screen is observed by completely dark adapted eyes. All trace of red color disappears from the neon light at intensities considerably greater than those resulting from sonic luminescence of the neon saturated (or air saturated) water. Therefore, the sonoluminescence in pure distilled water cannot be connected with activation of dissolved oxygen and we are probably dealing with electroluminescence from discharge in the cavitated neon, too faint to detect a red color. A similar electroluminescence occurs in nitrogen but it is still less intense.

Hydrogen is of special interest since it is an easily excited gas and one might expect to observe a sonoluminescence in hydrogen saturated water. However both Lenard¹⁷ and Thomson¹⁸ found that the waterfall potentials appearing where water is atomized in a hydrogen atmosphere are much less than in other gases. Therefore sufficient potential is not built up with cavitated hydrogen for a discharge to take place. The gas experiments definitely lead to the view that the sonoluminescence in pure water is balloelectrical in origin.

Effect of Dissolved Substances.—The sonoluminescence of distilled water containing air is remarkably independent of dissolved substances. Thus it is observed of nearly the same intensity¹⁹ whether acid (10% sulfuric acid, 0.1 *N* hydrochloric acid) or alkaline (10% potassium hydroxide, 0.1 *N* ammonium hydroxide, 0.1 sodium hydroxide); whether the salt content (and electrical conductivity) is high [saturated sodium chloride, saturated ammonium sulfate (rather bright), concentrated calcium chloride, "hypo"], medium (sea water) or low (tap water, 0.01 *N* potassium cyanide); in presence of heavy metals (1% copper sulfate, satd. mercuric chloride); of strong oxidants [dilute hypochlorite or hypobromite, potassium bichromate (faint), potassium persulfate, ferric chloride, acid cerium sulfate, potassium ferricyanide, 10% nitric acid, hydrogen peroxide] and strong reductants [sodium hydrosulfite, alkaline stannous chloride, ammonium sulfide (faint), 42% hydrazine hydrate (faint)]; of inert suspensions (zinc stearate, talc, infusorial earth, pumice and kaolin); of emulsions [mercury (rather bright), olive oil in dilute alkali]; of colloidal solutions (ferric hydroxide, starch),

of surface active substances (saponin, sodium glycocholate, soap, egg albumin); of peroxide inhibitors and developers (diphenylamine, hydroquinone, resorcinol, phloroglucinol, amidol, elon, pyrogallol) and dilute solutions of many other organic compounds (glucose, α -methyl glucoside, acetanilide, glycerol, ethylene glycol, ethyl and methyl alcohols).

The wide variety of conditions under which the sonoluminescence occurs, especially in either reducing or oxidizing solutions, is additional evidence against the view that the light is chemiluminescent in origin.

Relation to Other Luminescent Compounds.—Conditions which produce luminescence in cavitated water might conceivably excite fluorescence in solution. Very dilute fluorescein, eosin, erythrosin, rose bengale, cyanin, dicyanin A, pinacyanol chloride, rhodamin B, quinine sulfate,²⁰ uranyl nitrate, lophin and esculin were tested, but the luminescence was not *markedly* brighter than in pure water alone.

When insoluble fluorescent substances such as anthracene, salophen, salicylamide, natural willemite powder and phosphorescent zinc sulfide were suspended in water at 20° and subjected to supersonics, again not markedly greater luminescence appeared than in pure water. The salophen and salicylamide were also treated at 0° since low temperatures favor luminescence, but no *greatly* increased luminescence occurred.

In addition to being fluorescent in ultraviolet light, salophen and salicylamide are also triboluminescent, and lophin and aesculin are chemiluminescent when warmed with alkali in alcohol. Dilute pyrogallol (0.001 *M*) can be excited to luminesce in various ways,²¹ most easily by peroxidase and hydrogen peroxide, or by potassium ferricyanide and hydrogen peroxide, or by passage of ozone, but no brighter light appears when high frequency sound waves are conducted through dilute pyrogallol than in distilled water. Crude solutions of luciferin or luciferase from the luminous crustacean, *Cypridina*, also give the same intensity of sonoluminescence as pure water.

One chemiluminescent compound, aminophthalichydrazide, hereafter referred to as *luminol*, responds brilliantly to supersound waves, as first demonstrated for sonic treatment by Flosdorf, Chambers and Malisoff,⁶ who used it to detect the presence of active oxygen and of hydrogen peroxide formed from activated oxygen in cavitated gas bubbles reacting with water.

Sonic Chemiluminescence.—Aminophthalichydrazide and related compounds in alkaline solution, as shown by Albrecht²² and studied by numerous investigators, gives a brilliant bluish luminescence when oxidized in various ways (as by bromine water, ferricyanide or permanganate) and particularly in presence of active oxygen. Luminescence also appears at the anode of solutions containing luminol, electrolyzed with potentials of 0.5 v. or over; with hydrogen peroxide in presence (or absence) of catalysts; by bubbling of ozone (but not molecular oxygen); or even at metallic surfaces (Al, Zn, Cd) which dissolve in water with evolution of hydrogen and formation of hydrogen peroxide.²³ It is not surprising, then, to find

(17) Lenard, *Ann. Physik*, **46**, 584 (1892); **47**, 463-524 (1915).

(18) Thomson, *Phil. Mag.*, **37**, 341-358 (1894).

(19) It must be remembered that the intensity of weak lights cannot be estimated with any accuracy, even by completely dark adapted eyes.

(20) Somewhat brighter than water.

(21) Harvey, *J. Biol. Chem.*, **31**, 311-336 (1917).

(22) Albrecht, *Z. physik. Chem.*, **136**, 321 (1928).

(23) Harvey, *J. Phys. Chem.*, **33**, 1456-1459 (1929).

that this substance luminesces with relative brightness in the supersonic field even when shielded from all electrostatic influences.

The behavior of luminol solutions when saturated with various gases confirms the chemiluminescent origin of most of the light and in addition shows that the sonoluminescence of pure water has another origin than that of activated oxygen. In carbon dioxide there is no luminescence, since cavitation does not occur with the sound intensities available (and oxygen is absent). In pure hydrogen there is no luminescence since activated oxygen cannot form. In nitrogen (either purified by passing over red hot copper or mixed with 7% of hydrogen and passed over platinized asbestos) there is no bright sonic chemiluminescence of luminol but there still remains the faint sonoluminescence²⁴ which appears in pure water in absence of oxygen. In neon also the bright sonic chemiluminescence of luminol disappears but a faint luminescence remains similar to that in neon saturated water. Finally, if sodium hydrosulfite is added to luminol in a nitrogen atmosphere, there is no sonic chemiluminescence but only the sonoluminescence of water.

Therefore, we can conclude definitely that this compound shows a true sonic chemiluminescence when subjected to high frequency sound waves, as the result of the activated oxygen produced.

Temperature.—The sonoluminescence of water and also of solutions is brighter the lower the temperature and is quite marked at 0°. At 30° the intensity is considerably less than at 20° and above 40° there is practically no luminescence, although water at 90° will cavitate. It seems reasonable to suppose that the increased vapor pressure of water at high temperatures suppresses the discharge in the cavitated gas bubbles.

Luminol subjected to supersonics also luminesces more brightly the lower the temperature but the light is easily visible at 60° and does not disappear until a temperature of 85 to 90° is reached.

Hydrogen Peroxide and Luminescence.—Since hydrogen peroxide added to various substances can cause the emission of light and hydrogen peroxide is undoubtedly formed during sonic treatment of water, it seemed important to determine whether substances which combine with hydrogen peroxide or which catalyze the decomposition of hydrogen peroxide affect the sonoluminescence of water or the sonic chemiluminescence of luminol.

First it may be recorded that the mixing of hydrogen peroxide and water does not result in light emission nor does a brighter sonoluminescence appear in the subsequent mixtures than in pure water. I also have never observed luminescence during the decomposition of hydrogen peroxide, whether this is induced by inorganic catalysts (manganese dioxide, platinum black) or by catalase, and whether the decomposition is relatively slow or occurs (with catalase) with explosive violence. Therefore it appears that hydrogen peroxide can play little part in the sonoluminescence of water. Similar evidence is obtained from a study of hydrogen peroxide catalysts which might be expected to decompose hydrogen peroxide

before it could react further with possible emission of light.

Since catalase is a hydrogen peroxide catalyst so powerful that solutions of it showing no trace of color decompose hydrogen peroxide explosively, it was prepared²⁵ from beef liver by the method of Sumner and Dounce,²⁶ which involves extraction with dioxane. It was washed free of dioxane by half-saturated ammonium sulfate and dissolved in 0.1 *N* phosphate buffer at pH 7.4. This solution gave the usual sonoluminescence of water, although it decomposed hydrogen peroxide instantly.

When made slightly more alkaline and luminol added, the relatively bright sonic chemiluminescence of the luminol appeared of the same intensity as in a similar control tube without catalase. The catalase in the more alkaline luminol solution was found to be highly active in decomposing hydrogen peroxide. We are, therefore, led to the conclusion previously reached in sonic experiments by Flosdorf, Chambers and Malisoff⁶ that the luminescence of luminol is due chiefly to the activated oxygen rather than the hydrogen peroxide formed by the supersonics.

On the contrary, the oxidation of potassium iodide by supersonics is due largely to the hydrogen peroxide formed. Two tubes of potassium iodide, one containing catalase and the other not, were subjected to a supersonic field for one minute. Then starch solution was added to both. The tube with catalase gave only a trace of blue color while the one without catalase turned blue-black from the abundant liberated iodine and starch.

Ozone and Luminescence.—Although all observers report little if any ozone formed by supersonic treatment of water, it is possible that traces might form that are responsible for luminescence, since ozone passed through many organic substances will emit light. Ozone passed through distilled water or sodium chloride, bromide or iodide solution does not result in luminescence but if a trace of luminol is added, each bubble of ozone rising through the solution luminesces brilliantly. Therefore ozone cannot be concerned with the sonoluminescence of water but might add to the sonic chemiluminescence of luminol.

Inhibition of Sonoluminescence.—Although the sonoluminescence of water is remarkably independent of dissolved substances of various kinds (see a previous section), there are certain compounds which prevent its appearance. This was first noted in a study of sonoluminescence during emulsification by sound waves. It was observed that layers of water and mercury luminesced (somewhat brighter than pure water alone) when emulsified but layers of water and benzene did not. Therefore a systematic study was made of a number of fluids non-miscible with water. One drop of the liquid was added to 10 cc. of water.

It was found that propyl, butyl, amyl and capryl alcohols, ethyl butyrate, amyl acetate, ethyl ether, β , β -dichloroethyl ether, benzene and 1,4-dioxane prevented luminescence; that toluene, thiophene, petroleum ether and aniline allowed a faint luminescence, while carbon

(24) This faint luminescence was probably overlooked by Flosdorf, Chambers and Malisoff,⁶ who noticed no luminescence of luminol containing nitrogen in the sonic field.

(25) I am greatly indebted to Mr. R. G. Ballentine for the sample of pure catalase.

(26) Sumner and Dounce, *J. Biol. Chem.*, **121**, 417 (1937).

tetrachloride, chloroform, *o*-xylene, nitrobenzene, benzyl alcohol, paraffin oil, olive oil, *n*-butyl phthalate, bromoform and bromobenzene did not affect the sonoluminescence of water. With carbon disulfide in water the luminescence was brighter than with pure water alone.

When the above compounds are added to luminol solutions which are subjected to the supersonic field, only ethyl butyrate, aniline, benzene and ethyl ether completely quench the chemiluminescence. In chloroform and carbon tetrachloride the sonic chemiluminescence persists. This is due to the liberation of chlorine, as noted by Schmitt, Johnson and Olson³ in their study of chemical effects of supersound waves.

A survey of the liquids, non-miscible with water, which quench the sonoluminescence of water shows no obvious relation to other properties. The dipole moment may be zero or high and the vapor pressure at 20° may be great or small. Since the development of balloelectric potentials as well as electrical discharges in gases is markedly affected by various conditions, which have been incompletely investigated, it is not surprising to find a quenching of sonoluminescence by certain vapors.

Sonoluminescence of Halogens.—Of the many substances added to water and tested for luminescence at 20° during the present investigation, only bromine water emits a strikingly bright light (comparable to that of luminol) when subjected to supersonic fields. This is true even when saturated bromine water of a deep brown red color is tested. It is especially bright at 0° and faint at 40°. No luminescence was observed in pure bromine. Iodine dissolved in potassium iodide or in water does not luminesce in the supersonic field with any greater brightness than water at the corresponding temperatures, but chlorine water, although about as bright as distilled water at 20°, is decidedly brighter than pure water at 0°. Chlorine water and iodine dissolved in potassium iodide are very very faint at 40°. Just as in the case of pure water, the luminescence of these halogens is brighter the lower the temperature. When salts of these halogens are tested in dilute water solutions (sodium chloride and bromide, potassium iodide), the sonoluminescence intensity is like that of pure water.

The cause of the sonic luminescence of bromine water is of special interest. First it may be noted that bubbling oxygen or ozone through chlorine water, bromine water, or iodine in water does not result in the emission of light either at 20 or at 0°, nor does the addition of hydrogen peroxide to chlorine water, bromine water or iodine water, either with or without a catalyst (platinum black). There is also no visible luminescence at an anode of bright or platinized platinum when bromine water in dilute sulfuric acid is electrolyzed with potentials of 1.5 to 6 v. although the acid bromine water emits a bright sonoluminescence. Therefore the luminescence does not appear to be connected with any source of active oxygen.

A similar conclusion is reached from a study of dissolved gases. When pure hydrogen was bubbled through distilled water and over bromine to flush out the oxygen and the two then mixed in a hydrogen atmosphere and subjected to a supersonic field, the bromine water gave no trace of luminescence. However, if the same experiment is carried out with pure nitrogen, the sonoluminescence

in bromine water is just as bright as in air. Luminescence of the bromine cannot therefore be due to any reaction involving oxygen and must be a phenomenon similar to the sonic luminescence of water. Unfortunately no lines can be detected in the spectrum of the bromine water sonoluminescence but only a very faint band in the yellow region.

We now may inquire in more detail into the conditions under which luminescence may accompany cavitation of gas from liquids.

Reynolds Tube Cavitation.—Since water can be made to cavitate by other means than sound waves, it is of interest to look for luminescence in these cases also. A flask of water cavitates dissolved gas and also water vapor just before it boils; a ship's propeller cavitates the water just behind it as it revolves and may become badly corroded from effects of cavitation; water flowing through a constriction in a tube cavitates as a result of the increased velocity of flow and corresponding decrease in pressure, a Reynolds tube.²⁷ There are no records of luminescence about ship's propellers (apart from the luminescence of disturbed micro-organisms in the sea) and I have not been able to observe a trace of luminescence just before a flask of water boils.

In a Reynolds tube there is also no luminescence. This tube was made of glass 8.5 mm. internal diameter narrowing to 2.5 mm. and then expanding to 8.5 mm. again. It was attached to the water faucet and during flow beautiful cavitation with a hissing sound occurred but no trace of luminescence. A large Venturi meter (with a glass window), 5 in. (12.6 cm.) inside diameter narrowing to 2 in. (10.1 cm.) in the Engineering Building at Princeton University also was observed but no luminescence occurred during the abundant cavitation.

Luminol pumped through a Reynolds tube cavitates abundantly but exhibits no luminescence. Evidently the conditions for building up potentials and for activation of oxygen are very different in the sonic field from those in the Reynolds tube.

Preformed Gas Bubbles.—Although gas bubbles rising through a fluid are electrically charged, it is easy to demonstrate that already formed gas bubbles are not responsible for luminescence in the supersonic field. This experiment is carried out by exhausting the dissolved gas in a weak soap solution with a filter pump. In a tube in the supersonic field this solution does not luminesce, since it cannot cavitate. Then air is forced through a porous diaphragm into the solution while in the supersonic field. The minute bubbles, which are prevented from uniting by the soap film, travel upward, but no luminescence is visible until a certain amount of air has dissolved (after eight seconds). Then the newly air saturated solution cavitates and sonoluminescence appears. The air bubbles show beautiful aggregation as the result of sound wave pressure but not coalescence.

If a Reynolds tube of flowing water was placed over the vibrating crystal, there was no brighter luminescence around the minute bubbles of gas cavitated by the Reynolds effect than from other regions, although the bubbles immediately coalesce in the supersonic field. The experi-

(27) Reynolds, "Papers on Mechanical and Physical Subjects," Cambridge, Vol. II, 1901, p. 578.

ment shows conclusively that aggregation and coalescence of the gas bubbles cavitated by other means than supersonic does not lead to luminescence.

Duration of Sonoluminescence.—In order to determine whether any substance is produced with which luminescence is associated and which persists for even a short fraction of a second, the flow method of Hartridge and Roughton²⁸ was adopted. Water from the faucet flowed through a glass tube of 0.78 cm. internal diameter, touched to the oil over the vibrating crystal. With no flow, a faint sonoluminescence of water appeared in the tube. With increasing flow the light became brighter and remained bright up to a certain maximum flow when it began to flicker, first appearing then disappearing over the crystal. A slightly faster flow quenched the light permanently and there was no return of light until the rate of flow had decreased considerably. The fastest rate, just before the light permanently disappeared, corresponded to 100 to 150 ml. per second. For a diameter of 7.8 mm. this means that a column of fluid 200 to 300 cm. long would move past the crystal in one second. *The luminescence never spread even a few mm. beyond the edge of the crystal so that it could not have persisted over 0.001 second.*

By fusing a side-tube connected to a pressure gage to the flow tube it can be shown that the increased luminescence with low rates of flow is due to a slight increase in pressure (0.3 to 1.3 atm.) and the disappearance of the light at a certain rate of flow is due to increase in pressure to above 1.3 atm., which is itself sufficient to prevent cavitation and consequently luminescence (see next section). The disappearance of luminescence is not due to the velocity but to the pressure of water in the tube and we can say that there is no persistence of sonoluminescence with any rate of flow that can be attained by a pressure that allows cavitation. Luminol solution pumped through the glass tube over the crystal also shows no persistence of luminescence with a flow velocity of 130 cm./sec. The luminescence is brighter when the fluid is under slight pressure.

Pressure and Luminescence.—A study of the effect of pressure on sonoluminescence becomes a study of the effect of pressure on cavitation. A pressure chamber was constructed (Fig. 1) which consists of a brass tube with a glass test-tube sealed in one end with picene. At the other end is a cap with stopcock and at the sides a pressure gage and pressure piston are soldered on. The pressure apparatus is completely filled with water and the stopcock closed. By turning the screw thread of the pressure piston any desired pressure can be obtained. It must be emphasized that under these conditions the gas dissolved in the water in the pressure chamber is in equilibrium at atmospheric pressure and not at the pressure indicated by the gage. It was found that the luminescence (and cavitation) becomes intermittent at about 1.3 atm. and disappears at pressures above this figure. The light shifts to the top of the tube just before going out. When the pressure is decreased from above 1.3 atm., light does not again appear until it has reached about 0.8 atm. At slight pressure (0.3 to 1 atm.) the light is brighter than

with no pressure. This optimum pressure for sonoluminescence above atmospheric pressure, can be compared with the optimum pressure for supersonic cavitation to produce emulsification, observed by Bondy and Söllner.²⁹

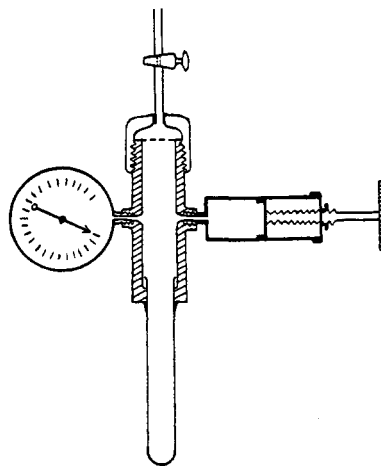


Fig. 1.

Under reduced pressure (in equilibrium with air at the same pressure) sonoluminescence of water is apparent until 31 cm. is reached, when no more luminescence appears and no cavitation is visible.

The sonic chemiluminescence of aminophthalichydrazide behaves under pressure as does the sonoluminescence of water since both are dependent on cavitation. The important fact is the increased luminescence under slight pressures.

Conclusions

The fact that sonoluminescence of pure water and bromine water occur in nitrogen but not in hydrogen is strong evidence for the view that the light is not the result of oxidation but is connected with the development of balloelectric potentials, since these are known to be large in nitrogen and small in hydrogen. The occurrence of luminescence in pure nitrogen shows definitely that activation of dissolved oxygen is not involved. No facts are directly opposed to the balloelectric discharge theory of sonoluminescence. We may therefore picture the minute bubbles of cavitated gas as developing a considerable electrical charge. When they collapse their capacity decreases and their voltage rises until a discharge takes place in the gas of the bubble, giving rise to a weak luminescence. The discharge may be thought of as occurring near the instant of complete collapse. Since velocity of collapse of the bubble would be favored by slightly increased hydrostatic pressures, it is not surprising to find the sonoluminescence intensity increased under slight pressures.

(28) Hartridge and Roughton, *Proc. Roy. Soc. (London)*, **B94**, 336-337 (1923).

(29) Bondy and Söllner, *Trans. Faraday Soc.*, **31**, 836-842 (1935).

If oxygen is present in the fluid, the discharge leads to activation, with formation of hydrogen peroxide or direct chemical reaction of activated oxygen with certain compounds present in solution such as aminophthalichydrazide. Sonic chemiluminescence then results, as shown by

Flosdorf, Chambers and Malisoff.⁶ Sonoluminescence is remarkably independent of substances dissolved in the water phase but is quenched by high vapor pressure of water (from rise in temperature) or by specific volatile organic compounds.

PRINCETON, N. J.

RECEIVED MAY 31, 1939

[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Oxidation of Carbonaceous Materials to Organic Acids by Oxygen at Elevated Pressures¹

BY R. C. SMITH, R. C. TOMARELLI AND H. C. HOWARD

Coals, cokes, and pitches yield significant amounts of organic acids when subjected to controlled oxidation with oxidizing reagents such as alkaline permanganate and nitric acid,² and small amounts of aromatic acids have also been isolated from oxidation products formed by the action of air, at elevated temperatures and pressures, upon suspensions of coal in aqueous alkali.³

In the present investigation oxidations were carried out in aqueous alkali at temperatures from 100 to 250° and oxygen partial pressures from approximately 100 to 375 pounds (7–25 atm.). Below 225°, reaction rate was very slow. Bituminous and anthracite coals and low temperature coke can be oxidized completely to carbon dioxide and water or to any desired intermediate stage. High temperature coke and graphite are partially oxidized under the same conditions, 50–60% of the carbon appearing as carbon dioxide, but much smaller amounts of organic acids are recovered. In the case of graphite no significant amount is obtained because mellitic acid is the principal organic acid formed in the oxidation degradation of these higher rank carbonaceous materials,⁴ and it has been found to be unstable under the conditions of this oxidation.

Increase in area of gas-liquid interface, by introduction of packing material into the bomb, has been found to increase significantly the reaction rate in the early stages of the degradation.

Of some nineteen different catalysts investi-

gated, only copper and cobalt salts affect reaction rate significantly, and these chiefly in the later stages of the oxidation.

Carbon balances show that under the proper conditions approximately 50% of the carbon of bituminous and anthracite coals can be converted to water soluble organic acids, the rest of the carbon appearing as carbon dioxide. Of the carbon recovered in the form of organic acids about one-fourth is oxalic acid and the balance aromatic acids. The actual amount of the latter recovered by oxidation of a Pittsburgh Seam coal was 30–40 g. per 100 g. of coal.

Experimental.—The oxidations were carried out in an all-nickel bomb of 1-liter capacity of identical design with those supplied for hydrogenation,⁵ except that a silver gasket was used. The bomb was heated externally by an electric furnace and agitated in the usual way by oscillation approximately 30° above and below the horizontal, about a transverse axis. Oxygen was introduced through a spiral of high pressure tubing from an oxygen reservoir of constant pressure. Since maintenance of the oxygen partial pressure depended upon absorption of the carbon dioxide formed, the amount of coal oxidized at one time was limited primarily by the amount of alkali which could be introduced. The maximum amount of coal which could be used was 50 g. and with materials of higher carbon content such as graphite it was necessary to reduce the size of the sample. The material to be oxidized was ground to –200 mesh and in most cases was suspended in a solution of 335 g. of potassium hydroxide in 350 cc. of water. In a few oxidations the potassium hydroxide was replaced by equivalent amounts of sodium hydroxide or calcium oxide.

In the early experiments considerable difficulty was encountered with the alkaline solution working back into the pressure tubing which supplied the oxygen. To prevent this a trap was provided in the pressure line just before it entered the head of the bomb and the line was continued inside the bomb and turned upward at the tip,

(1) Presented before the Division of Gas and Fuel Chemistry at the 96th meeting of the American Chemical Society, Milwaukee, Wisconsin, September, 1938.

(2) Bone and co-workers, *Proc. Roy. Soc. (London)*, **A110**, 537 (1926), **A127**, 480 (1930); **A148**, 492 (1935); Juettner, Smith, and Howard, *THIS JOURNAL*, **59**, 236 (1937); **57**, 2322 (1935).

(3) For a review of the work of F. Fischer and co-workers see Horn, *Brennstoff-Chem.*, **10**, 362 (1929).

(4) Juettner, *THIS JOURNAL*, **59**, 1472 (1937).

(5) American Instrument Company, Silver Spring, Md.