Chemistry

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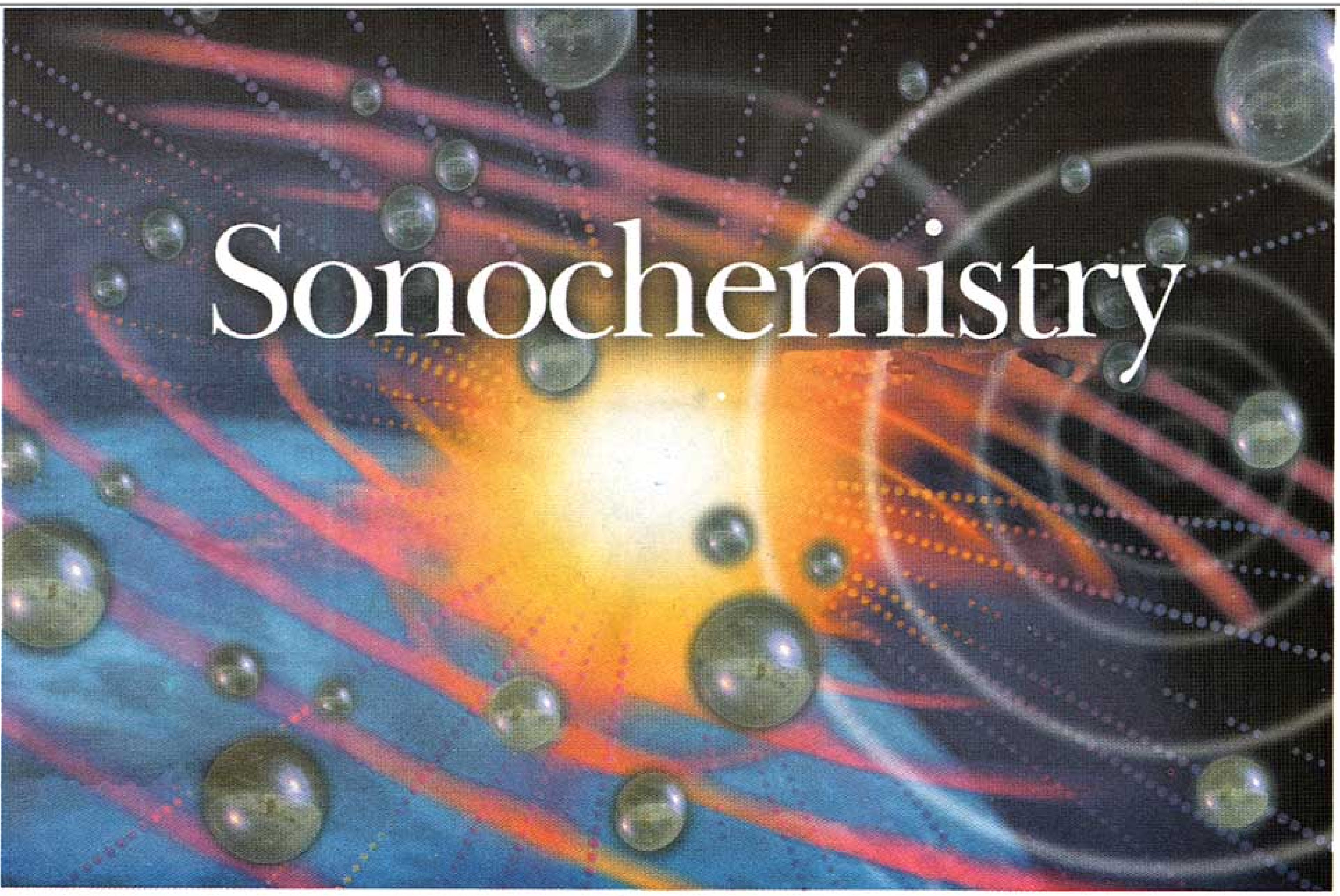

Chemistry

A quarterly newspaper for ACS members and science students focusing on the science and the people in chemistry.

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editorial

The director of a Hollywood movie calls and wants to rent your lab equipment for a few months. Props in a science thriller. The moving vans are on the way, Professor.

What's a chemist to do?

If you're Ken Suslick, you unload a storeroom full of junk, make a few bucks for your university, and get to see superstar Keanu Reeves use the gear in some very imaginative ways.

Suslick got the call a few years ago from the director of *Chain Reaction*, a 20th Century Fox tale of a Nobel laureate who uses sonochemistry to discover a limitless new source of energy. The director decided it might be nice to see a real chemistry lab before making the movie. Suslick agreed, and he gave the director a tour of his sonochemistry lab at the University of Illinois at Urbana–Champaign.

A couple of days later, the director called again, asking to rent Suslick's lab equipment for the movie set. Suslick patiently explained that they actually use the equipment, which is very expensive and delicate. Then it hit Suslick. The director doesn't need equipment that works, only stuff that *looks* like it works.

So, he invited the movie people back to check out a basement storage area filled with old Infracord spectrophotometers, black-and-white computer monitors, and other stuff that was once too good to junk but had become useless. They bite. Fox makes a $10,000 donation to the university. A moving van hauls the stuff to the movie set.

Two years later, Suslick and students munch popcorn at *Chain Reaction*'s first matinee and watch Keanu Reeves and associates beat them to the Big Breakthrough in sonochemistry research.

As Barbara J. Maynard points out in her article in this issue, there are big breakthroughs ahead in this relatively new branch of chemistry that uses ultrasound to drive reactions. From Maynard's descriptions, it's easy to understand why Hollywood featured sonochemistry in a thriller like *Chain Reaction*. Some aspects of the research really are fantastic, including sonoluminescence and the enormous temperatures and pressures created in sonochemical processes.

I average several hours a day on the World Wide Web, researching articles on science and just keeping current with new research. One of my longtime favorite science news sites is the award-winning ScienceDaily (**www.sciencedaily.com**) because of its content and ease of use.

Dan Hogan, the site's creator, is a regular contributor to *Chemistry*. He writes NewsBlast. We gave Dan another assignment for this issue: to describe the basics of starting and maintaining a Web site. Don't miss his informative and amusing article, especially if you have visions of setting up a dot-com site that pays for itself—and more.

Despite big strides in public understanding and appreciation of chemistry, the term "chemical" still makes a lot of consumers uneasy. Yes, it is irrational and unfair. Everything in the world is made from chemicals. Without synthetic chemicals, life would be short and miserable.

Pam Frost's article describes the new independent federal agency established to investigate accidents involving chemicals and recommend ways of improving chemical safety. There has been concern that the Chemical Safety and Hazard Investigation Board may exacerbate public concerns by focusing undue attention on the negative side of chemistry. Frost's report describes the board's formative period, when these concerns emerged, and its future role as a counterpart to the National Transportation Safety Board.

Forensic chemistry is the topic of CareerView in this issue. Robin Sussingham, another of our regular writers, describes why a life in crime can be so appealing as a first career or as a midcareer shift for chemists working in another field.

Cynthia Washam wrote the wonderful profile of Carolyn Bertozzi (ACS '90), a pioneer in chemical biology, because a reader suggested profiling Bertozzi for the Spotlight on ACS Member column. We're looking for names of more ACS members with interesting careers, significant contributions, or unusual interests out of the lab, office, or classroom. Send an e-mail with a few sentences about the person to **chemistry@acs.org**.

Among our other offerings are Web reviews, a full menu of ACS news, and our pal Lab Rat, who tackles a burning question.

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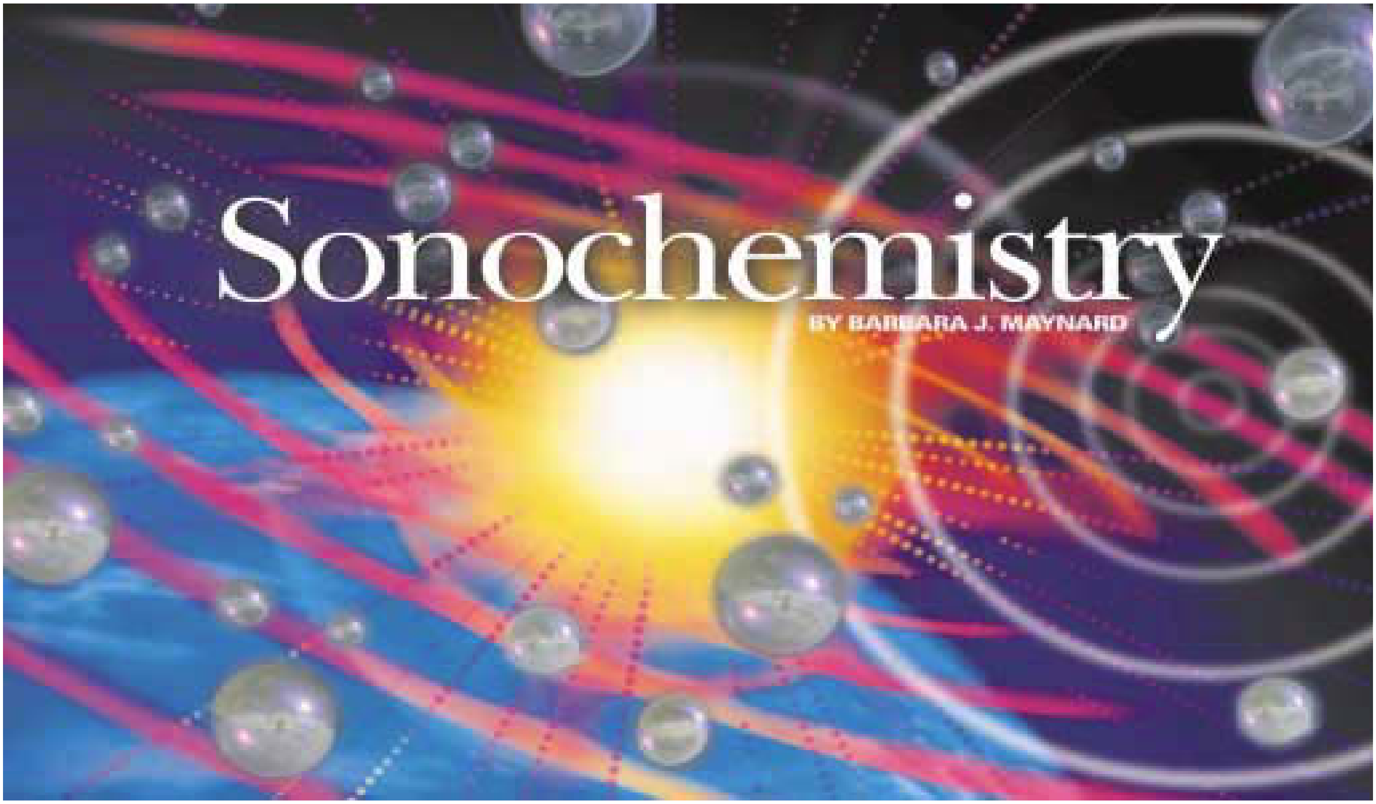
Michael Woods has received many national science writing awards, including ACS's Grady–Stack Award for Interpreting Chemistry for the Public.



Chemistry is the interaction of energy and matter. Yet there are surprisingly few ways of putting energy into molecules to drive reactions. One of the newest, ultrasound, uses the principles of acoustic cavitation in the formation, growth, and violent collapse of bubbles in a liquid.

Life as a sonochemist might not be quite as exciting as superstar actor Keanu Reeves suggested in the 1996 movie *Chain Reaction*. In that 20th Century Fox thriller, a Nobel laureate and his grad student discover a way of using sonochemistry to catalytically produce unlimited quantities of hydrogen from plain water—and get caught in a chain reaction of murder and high-tech espionage.

Unlike researchers in the movie, this real-life breed of chemists is constrained by realities such as the laws of thermodynamics. Even so, they are driving some very exotic reactions under extreme conditions. There are plenty of exciting practical applications—although not quite on a scale of the new source of clean, limitless energy described in *Chain Reaction*.

Sonochemistry is the emerging study of chemical reactions powered by high-frequency sound waves. Ultrasonic waves in liquids cause the formation of tiny bubbles that collapse so quickly, and with such enormous temperatures and pressures, that novel chemical reactions are generated. Chemists are using this unusual high-energy chemistry in many ways, such as creating inexpensive industrial catalysts, cleaning up polluted water, and zapping cancer cells.

BUBBLES HOTTER THAN THE SUN

Sonochemistry is based on the effects of cavitation, the creation and collapse of bubbles in a liquid subjected to ultrasound. Sound consists of alternating expansion and compression cycles traveling through a medium. Compression cycles push molecules together, while expansion cycles pull them apart. In a liquid, the expansion cycle of ultrasound can generate sufficient negative pressure to create bubbles, or cavities, in the liquid. Bubbles form at "weak spots", which are places where gases are either dissolved in the liquid or are trapped on contaminating particles. Even ultrapure liquids contain such weak spots, said Ken Suslick (ACS '75) the Lycan Professor of Chemistry at the University of Illinois at Urbana–Champaign—and props consultant for *Chain Reaction*.

"All liquids have particulates in them," he said. "Dirt is hard to get rid of. They are negligible in terms of chemical properties, but they are important in terms of physical properties." The negative pressure of expansion waves causes the gas to expand, creating a bubble. As the expansion cycle continues, the liquid surrounding the bubble begins to vaporize into the negatively pressurized cavity.

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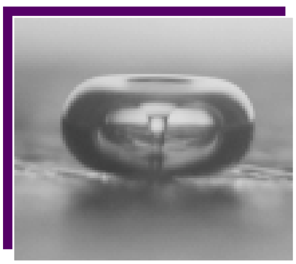
COURTESY OF K. SUSLICK.

Ken Suslick, University of Illinois at Urbana–Champaign.

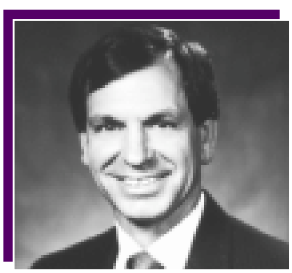
COURTESY OF M. HOFFMANN.

Michael Hoffmann, California Institute of Technology.



COURTESY OF L. A. CRUM

Cavitation near a solid surface can induce a microjet of liquid that streams through the bubble upon implosion.



COURTESY OF L. A. CRUM

Lawrence Crum, University of Washington.

from page 17

"It's somewhat similar to opening a carbonated beverage—it forms bubbles," explained Michael R. Hoffmann (ACS '74), a professor of environmental engineering science at the California Institute of Technology. "That's the carbon dioxide coming out of water making bubbles. In this other case, the ultrasonic field forces formation of bubbles, and it drives the gases in liquid phases into the bubbles. It also drives some amount of water vapor into bubbles."

The importance of cavitation for sonochemistry isn't so much how the bubbles form; rather, it is what happens when they collapse. At some point, a bubble can no longer absorb energy efficiently from the ultrasound, and it implodes. The rapid compression of gases and vapors inside the bubble creates enormous temperatures and pressures. Suslick and colleagues have estimated the temperature of these hot spots to be about 5000 °C, similar to the surface of the sun. The pressure is roughly 1000 atm, equivalent to the pressure at the Mariana Trench, the deepest point in the ocean.

Because the bubbles are so small compared to the volume of surrounding liquid, the heat dissipates rapidly, and ambient conditions remain essentially unaffected. Suslick and colleagues estimate that the cooling following collapse of a cavitational bubble is on the order of 10 billion °C/s. By comparison, plunging red-hot steel into cold water produces cooling on the order of a few thousand °C/s. This combination of high temperatures, high pressures, and rapid cooling creates conditions unattainable in other fields of chemistry.

The consequences of cavitation vary, depending on the materials involved. Cavitation occurring next to a solid surface has its own unique qualities. The presence of the solid makes the implosion asymmetric, with a jet of liquid forming on the side of the bubble opposite the solid. This microjet blows through the bubble at speeds approaching 400 km/h, a force strong enough to puncture metal plates.

Sir John I. Thornycroft and Sydney W. Barnaby first described this effect of cavitation in 1894. During trials of a new high-speed British navy ship, they attributed severe vibrations from and erosion in the propeller to the ability of turbulence to create imploding cavitational bubbles. In this case, the source of the cavitation was turbulence, but high-intensity ultrasound has similar effects.

In 1927, Alfred Loomis first noticed the unusual chemical effects of cavitation. In the ensuing decades, a handful of other chemists explored sonochemistry, but the field remained fairly quiet until the 1980s, when appropriate laboratory equipment became available. Today, some sonochemists use simple and cheap ultrasonic cleaning baths to generate low- intensity ultrasound, which is sufficient for many liquid–solid reactions, like Grignards or lithiations. For higher intensity ultrasonic fields, more powerful instrumentation is required, so some chemists use ultrasonic cell disruptors, which are common tools in molecular biology laboratories, to generate high-intensity ultrasound.

LIGHT IN A BUBBLE

Sonoluminescence—the creation of a tiny flame in a cool liquid—is an awesome part of ultrasonic cavitation. Sonoluminescent flames are light blue verging on ultraviolet—perhaps the only accurate scientific detail in *Chain Reaction*. Several competing explanations for the light exist, but Lawrence Crum of the Applied Physics Laboratory at the University of Washington said the only model that seems to fit is a plasma model, similar to conditions on the surface of the sun. According to this model, the inside of the bubble is a hot soup of detached electrons and parent ions generating plasma emissions as they bump into each other.

Crum studies ultrasonic cavitation from the perspective of a physicist. "Physicists are trying to find realms of matter or realms of nature such that other people haven't been there before," he said. "What we would like to do is to generate temperatures inside a sonoluminescent bubble that no one has ever achieved before. One of the things we're trying to do now is to make the bubble collapse with such intensity that the bubble gets so hot and the interior gets so hot, that we can get exotic physics out of it."

Crum and his co-workers study single-bubble sonoluminescence with the use of a lithotripter, the same device used to ultrasonically treat kidney stones. They hope to demonstrate that the light emissions observed when they collapse a bubble with a lithotripter indicate that they have achieved hotter temperatures than ever before. Some physicists hold out hope that conditions inside a cavitational bubble may be extreme enough to generate some type of fusion.

Although Crum is studying single-bubble sonoluminescence, chemists are typically more interested in understanding what happens with a cloud of bubbles. "There isn't enough matter inside a single bubble to be at all useful, from a chemist's point of view," Suslick said.

HOW HOT IS HOT?

Not surprisingly for such a young field, much remains to be resolved about the basic phenomena involved in ultrasonic cavitation. The temperature inside imploding bubbles, for example, is still hotly debated. Because the temperatures are far too fleeting for a thermometer to detect, Suslick and his colleagues have developed two different techniques to measure the temperature. First, they studied reactions for which they knew the dependency of rate on temperature. Comparing rates during cavitation to known values suggested a temperature of approximately 5200 K.

They confirmed their results by comparing sonoluminescent spectra with synthetic spectra. This method suggested a similar temperature of 5100 K. "Comparative-rate thermometry was the first way that anyone had made a legitimate temperature measurement. But it's not the easy way," Suslick said. "We were very fortunate to be able to find another way that works much more easily, and that's sonoluminescence. And even more fortunate that they gave the same answer."

Suslick and Crum both noted that these measurements do not necessarily reflect the maximum temperature possible in a bubble. "We only know what the emitting surface is like," Suslick said. "In some respects, this is like looking at a star. You can measure the surface temperature, but you're not really measuring the core temperature." Suslick pointed out, however, that temperatures inside imploding bubbles might be as hot as the inside of a star, but some physicists suspect there are much warmer temperatures yet to be detected.

PROTEIN MICROSPHERES

In just a few decades of existence, sonochemistry has found applications ranging from biomedical diagnosis to materials chemistry to environmental cleanup.

Tiny, air-filled balls have helped cardiologists around the world visualize the flow of blood through patients' hearts. Smaller than red blood cells, these balls are protein microspheres, produced by ultrasonic cavitation. Injected into the bloodstream, microspheres increase contrast in an echocardiogram—an ultrasound image of the heart—enabling the cardiologist to better diagnose a patient's condition.

Albunex was the first contrast agent approved by the U.S. Food and Drug Administration. Its walls are constructed of human serum albumin fused together by sonochemistry.

"The ultrasound is serving double-duty," Suslick said. "It's causing emulsification—that gives you the micron-sized droplets. And it's producing the oxidant sonochemically that's cross-linking the proteins to form a permanent shell." The cross-linked shell gives the microspheres a shelf life of several months but is readily broken down in the body by enzymes.

Microspheres also can be used for drug delivery. For example, the breast cancer treatment Taxol is difficult to administer because it's "not in the least bit water-soluble," Suslick said. Currently, patients endure lengthy intravenous drips for each dose. By filling protein-coated bubbles with Taxol, a single intravenous injection may be sufficient to administer the drug. "It goes from being in-patient to out-patient," Suslick said. This technology is currently in clinical trials. The advantage of using sonochemistry over other techniques for microencapsulation is that microspheres can be made with a biocompatible bubble, Suslick said. Other methods use synthetic polymers "that the body is not very happy with." Suslick and his co-workers hold 12 patents on potential uses for protein microcapsules, all in commercial development with American Bioscience.

BETTER MATERIALS THROUGH SONOCHEMISTRY

Materials chemistry has its own assortment of potential applications for sonochemistry. One is preparation of nanostructured materials—solids constructed from nanometer-sized building blocks. For example, amorphous metals, which have unusual magnetic, electronic, and catalytic properties, are formed through extremely rapid cooling—on the order of 1 million K/s—before crystallization can occur. The conditions of ultrasonic cavitation would seem ideal for this reaction, and in fact, Suslick and his team have succeeded in making amorphous iron, which has unusual magnetic properties and high catalytic activity.

Polymer degradation is another active field of research in sonochemistry. Cavitation cleaves bonds between component monomers, breaking polymers down into shorter chains of relatively uniform molecular weight. Because high-molecular-weight species are preferentially cleaved, this process can be used to control the size of desired polymers. In addition, cleaving bonds can create reactive macromolecules, which will react with other compounds to form copolymers.

Interestingly, polymer cleavage (and other reactions in a cavitational field) occurs more slowly at higher temperatures. This counterintuitive property makes sense, because at higher temperatures, more solvent vaporizes into the bubble, cushioning the collapse.

In addition to extreme temperatures and pressures, cavitational collapse also produces shock waves in the surrounding liquid. These waves have important consequences for reactions involving liquid–powder slurries. Powders are typically too small to generate the jets of liquid created by extended solid surfaces, but the particles can be slammed together by a passing shock wave. Suslick and associates estimated that the speed of impact is in the neighborhood of half the speed of sound. At these speeds, particles that hit each other directly can melt together. If the shock wave delivers a glancing blow, particles can abrade each other, smoothing each other's surface. This process can increase chemical reactivity of the powder by removing passivating coatings such as oxide. Metal slurries with melting points up to 3000 °C show this effect, indicating the temperature of these collisions.

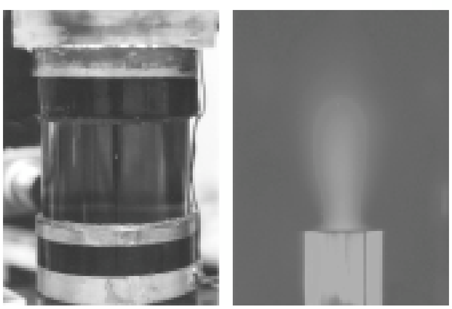
By removing passivating coatings, cavitation can make better catalysts. For example, ordinary nickel is a poor catalyst, but a porous form of nickel is an excellent catalyst. Unfortunately, the porous form of nickel is also expensive and environmentally problematic. After irradiation with ultrasound, ordinary nickel becomes 100,000 times more active, much like its pricey cousin, apparently because of the removal of its passivating oxide coating by interparticle collisions induced by shock waves.

SOUNDING OUT APPLICATIONS

Many of the applications described so far use organic liquids as a medium. In contrast, ultrasonic cavitation in water has its own unique qualities. "Water is fairly volatile and the products that you get from sonolysis of water, hydrogen atoms and hydroxyl radicals, are extremely reactive and so they dominate the chemistry," Suslick said.

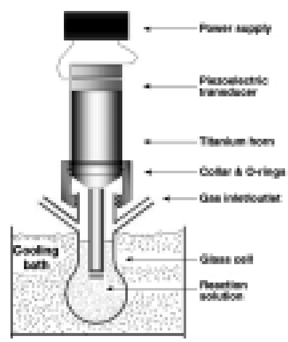
Some chemists are putting the free radicals generated by aqueous cavitation to work in a variety of applications. For example, ultrasound may soon be used to remediate contaminated water. Suslick painted the picture of a rural farmhouse with pump water polluted with a few parts per million of pesticides: "How do they clean up the water for drinking or bathing? They have a few choices, and basically, none of them are very good." While ultrasonic water purifiers are not yet commercially available, the technology is ready, Hoffmann pointed out. He has been studying ultrasonic cavitation as a way to clean up contaminated water since the mid-1980s. A graduate student sparked the

COURTESY OF L. A. CRUM.

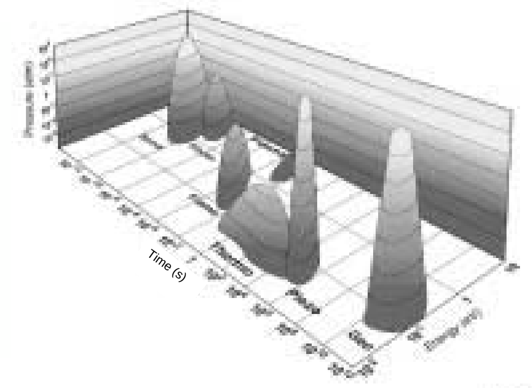


Single (left) and multiple bubble (right) sonoluminescence. The figure on the left shows a single, acoustically levitated sonoluminescent gas bubble. The figure on the right shows an acoustic horn transducer, radiating into a liquid and creating many gas bubbles that emit light during collapse.

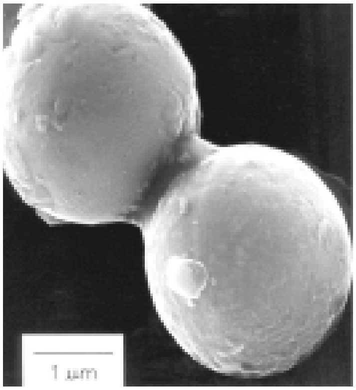
COURTESY OF K. SUSLICK.



Typical sonochemical apparatus.

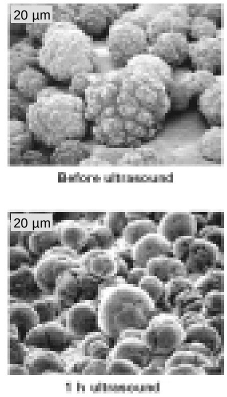


Sonochemistry consists of high-energy reactions under high pressures and short times.



COURTESY OF K. SUSLICK.

Two particles of zinc fused together after ultrasonication.



Nickel powder before and after ultrasonication.

idea by suggesting they try ultrasound as an alternative means to generate hydroxyl radicals. Ever since, Hoffmann has continued to work with ultrasound and other methods for water remediation. His research on the chemistry behind acoustic degradation of contaminants has demonstrated that free radicals formed by water decomposition are only one component of the process.

"If you have localized temperatures of 4000 to 5000 K, you'll pyrolyze a lot of compounds, especially more volatile ones that enter the vapor phase of the bubble," Hoffmann said. "Once you get a radical by pyrolysis, it can react with oxygen to initiate a free radical process that the hydroxyl radical would have initiated."

Hoffmann suggested a third possible factor. "We have been exploring the notion of supercritical phase reaction. That is when water is above 374 °C and 220-atm pressure for some period of time. It's above the critical point, which means it exists simultaneously as water and a vapor. ... Its properties change pretty dramatically under these conditions."

One common pollutant that could be remediated by ultrasonic cavitation is pentachlorophenol (PCP), a U.S. Environmental Protection Agency priority pollutant and a suspected carcinogen that has been widely used as a wood preservative and biocide. Hoffmann and his co-workers have been exploring the effects of ultrasound intensity and frequency and determining the kinetics and mechanism of sonolytic degradation of PCP.

Biomedical researchers are using ultrasound in a very different aqueous environment—animal tissues. Sonodynamic therapy may someday use the synergistic effects of ultrasound and drugs known as sonosensitizers to fight cancer. Ultrasonic irradiation can activate porphyrins and other sonosensitizing agents—drugs with antitumor activity when irradiated in rodents. The mechanism underlying this phenomenon is still uncertain. But Peter Riesz (ACS '52) of the Radiation Biology Branch of the National Cancer Institute, National Institutes of Health, and Vladimir Misik of the Institute of Experimental Pharmacology, Slovak Academy of Sciences, recently proposed that peroxyl radicals are likely to be the cytotoxic agent. According to their model, cavitation breaks the sonosensitizers into free radicals, which then react with oxygen to form peroxyl radicals. The peroxyl radicals travel to the membrane of nearby tumor cells, inflicting damage and killing the cells. Sonodynamic therapy may prove useful for cancer treatment because ultrasound can penetrate deeply into tissues and can be precisely targeted, limiting unintended effects.

The list of potential applications of ultrasound for the chemical industries goes on and on. For example, Suslick noted that ultrasound can force dyes to penetrate more deeply into leather, eliminating the obvious scratches that appear on the superficially dyed leather available today. Other applications under development include electroplating, microelectronic wafer processing, and high-strength, light-alloy production. "The applications of sonochemistry itself are going to be with high value-added materials: pharmaceuticals, catalysts, high-value inorganic materials, perhaps," Suslick said. In the meantime, there is plenty of basic research to be done… and better movies to be made.

FOR MORE INFORMATION

- Kenneth S. Suslick, University of Illinois at Urbana–Champaign
  www.scs.uiuc.edu/~suslick
- Applied Research and Technology Group
  http://pluto.apl.washington.edu/artg/acelpsol.html
- National Institutes of Health
  http://search.nci.nih.gov/s97is.vts
- Michael R. Hoffmann, California Institute of Technology
  www.its.caltech.edu/~ees/hoffgroup/research.html

COURTESY OF J. SOSTARIC.

Vladimir Misik, Slovak Academy of Sciences, and Peter Riesz and Joe Sostaric, National Institutes of Health (left to right).

Barbara J. Maynard is a science writer in Laporte, CO.