

Ultrasound Proves To Be A Versatile Tool For Chemists

Illinois chemists fmd some chemical uses for sound pitched above 16 kHz, such as controlling chemical reactions, creating unusual materials

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Ultrasound affects people's lives in various ways, notes Kenneth S. Suslick, a chemistry professor at the University of Illinois, Urbana-Champaign. Ultrasound shows up in such varied uses as medical imaging, and self-focusing cameras, he points out. "But," he adds, "we are only now discovering how useful ultrasound is in controlling chemical reactions and creating unusual materials."

As evidence for the growing and varied usefulness of sonochemistry, Suslick, whose specialty is sonochemistry, cites the appearance of three articles by him and his co-workers in three prestigious scientific journals, all published within the space of a month. One, in *Science*, deals with measuring the temperature of cavitation, the phenomenon at the heart of sonochemistry. A second, in *Nature*, reports the use of ultrasound to create an amorphous metal powder. The third article, in *Proceedings of the National Academy of Sciences*, describes how ultrasound has helped explain the behavior of air-filled proteinaceous microbubbles used as contrast agents in sonography.

Ultrasound is sound pitched above 16 kHz, beyond the normal range of human hearing. With appropriate transducers, scientists can make narrow, focused beams of ultrasound "more intense than the roar of a jet engine," Suslick says. The chemical effects of ultrasound

derive from the creation, expansion, and collapse of small bubbles that result when a liquid is irradiated by an ultrasonic beam.

This process, called cavitation, creates intense heat in certain spots within the liquid. But the surrounding liquid cools the hot spots quickly, in less than a millionth of a second. "There is tremendous local heating and emission of light," Suslick says. "It's a microscopic flame in a very cold liquid. The temperature tells us what kind of chemistry we can expect." However, until now there had been no unambiguous experimental answer to the vital question, "How hot is it?"

Suslick and former graduate student Edward B. Flint (now an assistant professor of chemistry at Wittenberg University) have provided the answer, at least for one silicone oil, using sonoluminescence as a spectroscopic probe [*Science*, 253, 1397 (1991)].

Although theoretical hydrodynamic models have been used to calculate the temperature of cavitation, the models have been very sensitive to assumptions, and the temperature predictions have varied from as low as 1000 K to more than 10,000 K. Most earlier efforts to measure the temperature experimentally have also been unreliable.

More than five years ago, Suslick and coworkers measured of the temperature of sonochemical reactions that, under the conditions of the experiment, yielded a value of 5200 ± 500 K for the gas phase of cavitation. However, the measurement involved "laborious" analyses and required "substantial extrapolation of kinetic parameters."

In the current more direct approach, Suslick and Flint developed a scheme for temperature measurement adapted from flame and plas-

ma techniques and based on the rotational and vibrational fine structure of diatomic emission spectra. Specifically, they use medium resolution sonoluminescence spectra from excited-state diatomic carbon.

Suslick notes that emission from the "Swan bands" of diatomic carbon can be seen in many organic liquids under ultrasonic irradiation. The silicone oil was chosen because of the high intensity of its sonoluminescence. However, the medium-resolution spectra didn't permit the use of the common methods of calculating spectroscopic temperature.

Instead, the Illinois chemists used "well-understood theory of diatomic molecule emission" to develop a series of synthetic spectra. Spectra were generated for vibrational and rotational temperatures ranging from 4500 to 5500 K. Comparison of the synthetic spectra and the experimentally determined sonoluminescence spectra showed the latter corresponded to an effective cavitation temperature of 5075 ± 156 K. Incidentally, Suslick says, the good match between synthetic and experimental spectra provides definitive proof that sonoluminescence is a thermal process and not an electrical discharge process.

The temperature determined from the sonoluminescence spectra is within the error limits of the earlier sonochemical measurements. However, Suslick notes, there were "significant experimental differences" in the two studies. For example, the vapor pressure was much lower in the sonoluminescence determination than in the earlier experiment. The lower vapor pressure might have been expected to increase the cavitation temperature, but it did not. That suggests "there may be an experimental upper limit to temperature obtainable during cavity collapse."

Turning from analysis to synthesis, Suslick notes that sonochemical techniques have recently been used to synthesize amorphous iron powder [*Nature*, 353, 414 (1991)]. He relates that the "metallic glasses" such as amorphous iron, have remarkable electronic, magnetic, and corrosion-resistant properties. These properties make them potentially useful for industrially important applications including transformer cores, audio and videotapes, and corrosion-resistant coatings. In addition, some of the amorphous metals and alloys can act as catalysts.

However, Suslick says, amorphous metals are hard to make, because molten metals must be cooled at rates of about 10^5 to 10^7 K per second to prevent crystallization. To put those numbers into perspective,

when red hot steel is plunged into cold water, it cools at a rate of only about 2.5×10^3 K per second.

Suslick recognized that the acoustic cavitation that takes place when a liquid is ultrasonically irradiated affords the rapid heating and cooling rates needed to form metallic glasses. Earlier sonochemical work at the University of Illinois had indicated that the hot spots created by cavitation could reach temperatures of about 5200 K, with calculated lifetimes of less than two microseconds. Recent sonoluminescence experiments by other scientists suggest the lifetimes may be as short as one nanosecond or even less, Suslick says. Thus, he calculates the heating and cooling rates during bubble collapse are at least 2×10^9 K per second; they may even reach 10^{13} K per second.

Accordingly, Suslick, working with postdoctoral associate Andrzej A. Cichowlas, former postdoctoral associate Seok-Burm Choe, and graduate student Mark W. Grinstaff, embarked on an experiment to determine the merits of the approach. The Illinois chemists subjected iron pentacarbonyl to high-intensity (20 kHz, 100 watts per sq cm) ultrasonic radiation for three hours. The pro-

cess yielded a dull black powder (in "gram quantities," Suslick observes) that was then filtered and washed. Elemental analysis revealed the powder to be 96% iron by weight, with traces of carbon and oxygen.

The iron powder has been examined with a number of methods, including scanning and transmission electron microscopy, differential scanning calorimetry (DSC), x-ray powder diffraction, and electron beam microdiffraction. All the tests confirmed the amorphous character of the powder, Suslick says. For example, transmission electron micrographs revealed no sign of crystallite formation to below 4 nm. DSC showed a large exothermic transition at 308 °C, indicating the amorphous iron had crystallized.

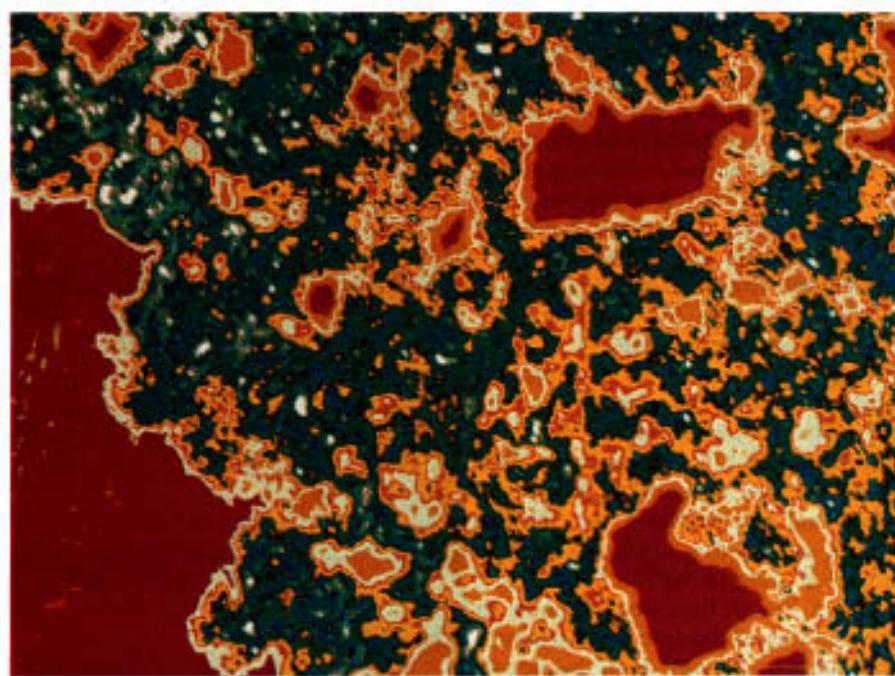
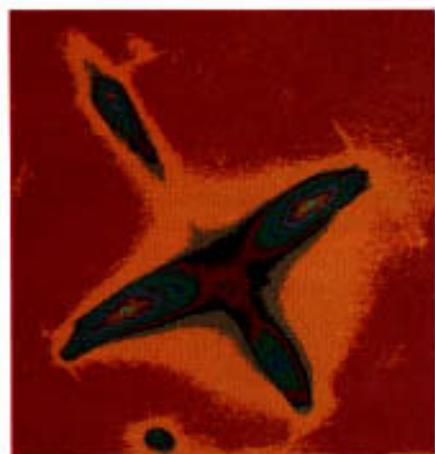
Similarly, x-ray powder diffraction studies of the original powder showed no diffraction peaks. After the powder was heated to 350 °C, x-ray powder diffraction did show characteristic α-iron lines. However, Suslick says, the patterns revealed no other iron-based peaks, indicating the powder was essentially pure iron. Earlier iron-containing metallic glasses had included significant levels, he adds, typically more than 20% of other elements.

Other tests showed the powder to be highly porous, with surface areas of the order of 120 square meters per g. That's about 150 times greater than the surface area of commercially available iron powders, Suslick says. Heated to 350 °C, the powder sinters and becomes metallic in color, indicative of crystallization. And its surface area decreases, becoming comparable to that of the commercial crystalline iron powder.

The amorphous iron powder catalyzes at least two industrially important reactions—the hydrogenation of carbon monoxide (the Fischer-Tropsch process) and the hydrogelysis-dehydrogenation of saturated hydrocarbons. Suslick notes that the Fischer-Tropsch conversion takes place at 200 °C, and that the amorphous iron powder is 10-fold more active (on a weight basis) than the commercial powder.

Similarly, catalytic activity at 250 °C for dehydrogenation of cyclohexane to benzene and subsequent hydrogelysis (mostly to methane)

Cavitation temperature determination test (left); electron micrograph of sonochemical synthesis of amorphous iron powder (below)





Suslick: now finding uses

was more than 30 times greater for the amorphous iron powder than for the crystalline. Suslick attributes the increased reactivity in large part to the large surface area of the amorphous iron. "As expected, sintering and crystallization of the metallic glass powder at [greater than] 300 °C significantly decreased its catalytic activity," he notes in *Nature*.

Turning from synthesis to elucidation of mechanisms, Suslick says

that ultrasound has helped explain how proteinaceous microbubbles are made [Proc. *Natl. Acad. Sci. USA*, 88, 7708 (1991)]. He notes that long-lasting air-filled microbubbles can be made by ultrasonic irradiation of aqueous solutions of proteins. The microspheres are useful as echo-contrast agents for such medical applications as sonographic imaging of the heart.

What wasn't known was how the microbubbles were formed and what held them together. Suslick, again working with Grinstaff, found ultrasound does "double duty." First, it disperses small droplets of air into the solution, a physical phenomenon. Then, and perhaps more importantly, ultrasound makes the microbubbles long-lasting by forming interprotein crosslinking of cysteine residues. The principal crosslinking agent, Suslick says, is superoxide, created by the extremely high temperatures produced during acoustic cavitation.

Suslick notes that all three projects were supported by the National Science Foundation. The National Institutes of Health provided some of the funding for the microbubble work.