Kinetics at the Critical Point of Fluids

Changes in solvent properties near the critical point may influence reaction rates, but a key experiment is shown to be wrong

A 19-year-old experiment that purports to show a dramatic slowing of a chemical reaction when that reaction is carried out near the critical point of a fluid has been shown to be incorrect. The original experiment had stimulated theoretical studies of the effects of critical phenomena on chemical reaction rates, but that theory has since proved highly controversial. The new experiment is not likely to settle the controversy, but it may stimulate a new interest in the effects of critical phenomena on chemical reactions.

The study of critical phenomena has undergone a renaissance among physicists during the last decade. Theoretical studies by Kenneth Wilson of Cornell University and others have shown that a wide variety of seemingly disparate phenomena can be encompassed within a single theory. Such phenomena include: the Curie point, the temperature above which a ferromagnet loses its magnetization; the superconducting transition temperature, above which superconductivity is destroyed; the order-disorder temperature, above which the ordered arrangement of metal atoms in some alloys disappears; and the critical point in fluids, the temperature above which a pure fluid can exist in only one phase, regardless of the pressure applied to it. That renaissance culminated in the award to Wilson of the 1982 Nobel Prize for Physics.

Chemists, however, have shown little interest in critical phenomena, despite the fact that many properties of solvents can change dramatically near the critical point. The heat capacity and the compressibility of the solvent increase sharply near the critical point, for example, while the diffusion constant drops markedly. These factors have the potential to change the rate and equilibrium constants for chemical reactions; such changes might, in turn, lead to new understanding of the thermodynamics and kinetics of chemical reactions in solution, fundamental properties that are still poorly understood despite intensive theoretical and experimental studies.

Only a few reactions have been studied near critical points, and most of these have shown only modest changes in reaction rates or in the rates of phenomena such as proton transfers. These small changes, says Sandra Greer of the University of Maryland, "are of little interest to experimental chemists, but of great interest to theoreticians."

One experiment was different, however. In 1966, I. R. Krichevskii and his colleagues at the Moscow Institute of the Nitrogen Industry reported on the photolytic dissociation of cholorine in a sealed vial at a temperature near the critical point. Below the critical point, the chlorine exists in two phases separated by a meniscus. Upon irradiation, the meniscus disappeared; the investigators attributed this disappearance to a decrease in the critical temperature resulting from dissociation of the chlorine.

When irradiation was halted, Krichevskii and his colleagues observed that it took 70 to 80 minutes for equilibrium to be reestablished in the system. They concluded that this effect was caused by a near cessation of diffusion at the critical point, which slowed the recombination of the chlorine atoms. Because chlorine atoms normally recombine in a time on the order of picoseconds, their results implied a slowdown of about 14 orders of magnitude.

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Greer attempted to reproduce the Russian work as part of her own studies on chemical equilibria near the critical point. In a paper accepted for publication in *Physical Review A*, she reports that the Soviet group apparently measured thermal relaxation of the system rather than recombination of chlorine atoms. By monitoring changes in polarizability of the fluid which occur upon dissociation and recombination of chlorine molecules, she was able to show that two separate processes occur. One is a thermal relaxation, like that measured by the Soviets, which occurs over a period of about an hour. The second is the chemical recombination of chlorine atoms, which occurs in a period shorter than seconds. Greer was unable to measure the actual recombination time because the apparatus was not designed to study very fast reactions. It is thus still possible that there is a slowing of the reaction rate near the critical point but that the magnitude is much less than the Soviets had claimed.

A theoretical underpinning for the rate slowing has been provided by Itamar Procaccia of the Weizmann Institute of Science and Moshe Gitterman of Bar-Ilan University in Ramat-Gan, Israel, although their results do not predict the magnitude of the slowing. Grossly simplified, their calculations predict that, when all or all but one of the components of a mixture participate in a reaction, a deviation of the system from its chemical equilibrium does not create a thermodynamic restoring force. The forward and backward reactions continue to proceed at almost the same rate as in equilibrium, in spite of the change in concentration. The observed reaction rate, which is the difference between these two reaction rates, vanishes. When more than one component of the mixture does not participate in the reaction, the effects are less dramatic and the rate can increase, decrease, or remain unchanged.

That view is disputed by Paul Martin of Harvard University who has written a manuscript on the topic but not yet submitted it for publication. He argues that approach to the critical point will affect only the slowest process occurring in the system; in most real systems, the slowest processes will be thermal or acoustical conduction, so that the rate of the chemical reaction will not be affected. In fact, Greer did observe a deviation of thermal relaxation from what would be expected in a noncritical fluid.

In contrast, Steven Adelman of Purdue University argues that there can be a major effect on chemical reaction rates near the critical point. These effects, he says, will be mediated by changes in the solvation shell around the reactants. Both Adelman and Martin, however, agree that further experiments need to be conducted to observe actual effects near the critical point. Only then will it be possible to rationalize theory and experiment.—**Thomas H. Maugh II**