Phenomenal fluids

Supercriticality

A strange and intriguing state in which solids can dissolve in gases, and liquids can alternate between reflectivity and transparency.

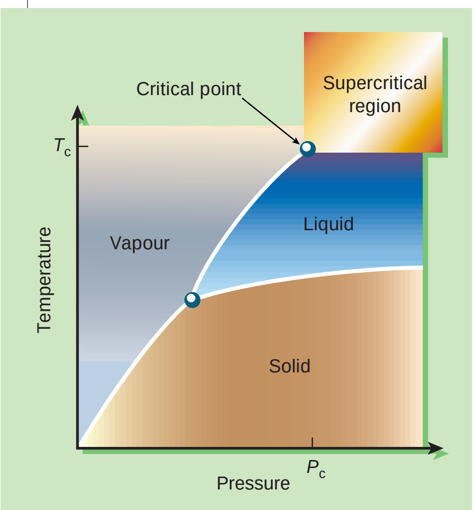
Martyn Poliakoff and Peter King

Heat a liquid in a sealed tube; it seems a simple enough experiment. But it has intrigued chemists and physicists for over 175 years, probably because the results are unexpected, almost counterintuitive.

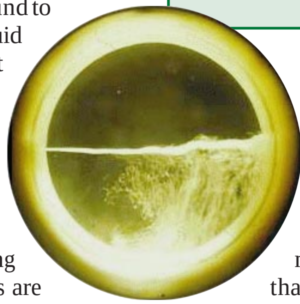
What you see depends on how much liquid is in the tube. If the tube is almost empty, the liquid evaporates quickly and you are left with a gas at moderate pressure. If it's almost full, the liquid expands rapidly to fill the whole tube and the pressure rises alarmingly. Put in just the right amount, and the meniscus grows faint and disappears abruptly: the contents of this tube have passed through the 'critical point' and become 'supercritical'.

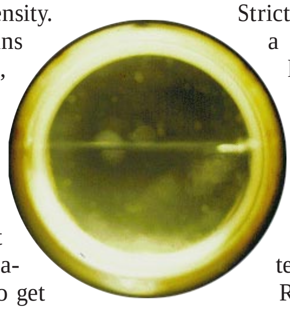
If you heat the tube more slowly, the liquid begins to look opalescent as it approaches its critical point. As the opalescence increases it grows redder and darker and, if you have judged things really well, goes completely black. At the critical point, it becomes perfectly reflecting and you see your own eye staring back at you. Heat it a bit more and the fluid passes back through red to become completely transparent again. Now, perhaps you see why supercritical fluids (SCFs) have fascinated people for so long. A pure substance in a sealed tube turns black merely because of a tiny increase in temperature — in some cases an increase as small as one-hundredth of a degree.

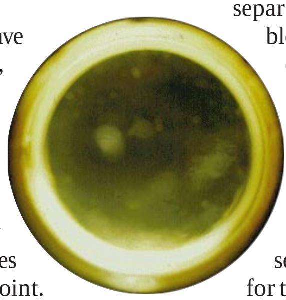
Opalescence arises because the compressibility of the fluid at the critical point is infinitely high. When this happens the microscopic thermal fluctuations that occur naturally in any fluid become strongly correlated, leading to large-scale, coherent density fluctuations. These large density fluctuations are very effective at scattering light. The high compressibility and the correlated fluctuations also cause the speed of sound to drop to a minimum as the fluid passes through the critical point and the fluctuations attenuate the sound. In 1822, these acoustic effects were exploited unwittingly by Cagniard de la Tour when he heated alcohol in a sealed gun barrel and listened to the musket ball rolling about. Acoustic measurements are still important for studying SCFs: we have been using them to locate the critical points of chemical reaction mixtures.



Critical conditions: above, phase diagram for a pure substance showing the critical pressure, P_c, and temperature, T_c. Above right, the effect of heating CO_2 rapidly through the critical point from liquid (top) to supercriticality (bottom).







The whole tube is now filled with a supercritical fluid of uniform density. Technically it's a gas, but it retains some properties of a liquid, including the ability to dissolve many solids. The idea that solids can dissolve in gas is so surprising to some scientists that, on first hearing of it, they fondly imagine that SCFs might dissolve substances that generations of chemists had failed to get into solution. In reality, supercritical CO_2 ($scCO_2$), the most common SCF, has a solvent power similar to that of petrol — although it does have the unusual ability to dissolve fluorinated organic compounds.

In recent years, industries have used SCFs, particularly $scCO_2$, as solvents for applications ranging from the extraction of caffeine, scents and essences to the degreasing of machine components. The handy thing is that the solubility of many compounds in CO_2 changes markedly near the critical point. Lower the temperature or pressure by a small amount and it may well start snowing caffeine or even grease, and the CO_2 can be reused or released back into the atmosphere.

There is increasing interest in SCFs, particularly $scCO_2$, as environmentally acceptable solvents for chemical reactions. But SCFs are attractive to chemists for reasons other than environmental friendliness. SCFs can provide reaction conditions that may lead to enhanced rates or alternative reaction pathways to those offered by conventional solvents. Supercritical water is so reactive that materials ranging from paintshop waste to nerve-gas weapons are rapidly converted into a few harmless oxides, water and CO_2. In many cases, reaction products may be extracted by making tiny reductions in pressure or temperature.

Chemical reactions involve mixtures, and the critical behaviour of mixtures may be far more complicated than that of a pure substance, with two or more liquid phases as well as the gas phase. The challenge in controlling the reaction often lies in characterizing and using this complex behaviour.

Strictly speaking, the critical point of a mixture is reached when the liquid and gas phases coalesce and the densities of the two phases are equal at the moment of coalescence. In practice, any homogeneous mixture at a temperature above the critical point of the pure solvent is termed 'supercritical'.

Returning to the sealed tube, what happens when our simple SCF is rapidly cooled? While it is supercritical, the fluid has a uniform density in the tube; therefore, as it cools through the critical point and separates into two phases, gas bubbles and liquid droplets form with equal probability throughout the tube. The droplets begin to fall and the bubbles rise. A veritable storm erupts — quite different from the gradual disappearance of the meniscus when the liquid is heated. In short, a second beautiful phenomenon for the price of one!

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FURTHER READING

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http://www.nottingham.ac.uk/supercritical