9.10: Supercritical Water

At temperatures exceeding 374.4°C and an extremely high pressure of at least 217.7 atm (217.7×normal atmospheric pressure) the distinction between liquid water and vapor vanishes and water enters a special physical state called a **supercritical fluid**. As a supercritical fluid, water no longer has the abundance of hydrogen bonds that give liquid water its special properties and that make it such a good solvent for ionic materials; instead, it becomes a good solvent for organic materials. The properties of supercritical water can be changed over a wide range by varying temperature and pressure and conditions can be attained in which the water is completely miscible with nonpolar compounds while retaining its ability to solubilize ions and polar species. Varying the pressure on supercritical water can change its density continuously from gaslike to liquid-like with a corresponding variation in the properties of the fluid. Although the conditions required to maintain water as a supercritical fluid are very severe and require special equipment, its ability to substitute for organic solvents make supercritical water very useful for a number of purposes, such as a medium for organic synthesis reactions. Even when compressed to a density equal to that of liquid water, supercritical water has a low viscosity. This is important for chemical processes because it increases mass transfer and rates of diffusion in diffusion-controlled processes.

Supercritical water has enormous potential as a solvent medium and catalytic material for chemical reactions. Its high temperature is conducive to pyrolysis, it promotes the hydrolysis of compounds in which molecules are cleaved with addition of H_2O, and in the presence of O_2 and other oxidants it is a strongly oxidizing medium. Careful tuning of temperature, pressure, and oxidant levels enables supercritical water to facilitate partial oxidation of organic materials such asthe partial oxidation of methane to produce methanol:

$$\mathrm{CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH} \tag{9.10.1}$$

Whereas methane must be moved by pipeline or as an extremely cold cryogenic liquid, which is hard to do from some of the remote regions where natural gas is found, methane converted to liquid methanol can be shipped in large tankers and used as a motor fuel or in fuel cells.

Oxygen, like other common inorganic gases, is completely miscible with supercritical water under extreme pressures, which increases its capability to act as an oxidant in chemical synthesis and waste destruction. Supercritical water is an excellent medium in which to use dissolved molecular oxygen to oxidize organic wastes including chlorinated compounds to carbon dioxide, water, and inorganic halides (chloride ion). The process is facilitated by the ability of supercritical water under certain conditions to act as a good solvent for organic wastes such as polychlorinated biphenyls (PCBs).

Under the extreme pressure and temperature conditions of around 30 km in the geosphere water is likely to be supercritical. In the presence of supercritical water at these depths, minerals may behave much differently compared to their behaviors under normal conditions, especially with respect to their dissolution and precipitation behavior. There is also evidence to suggest that chemical processes may form methane under these conditions leading to a non-biological pathway for hydrocarbon formation.