Heavy Water

Given that the boiling point of D$_2$O is 101.4 °C (compared to 100.0 °C for H$_2$O), evaporation or fractional distillation can be used to increase the concentration of deuterium in a sample of water by the selective removal of the more volatile light water, H$_2$O. Thus bodies of water that have no outlet, such as the Great Salt Lake in Utah, USA and the Dead Sea in the Jordan Rift Valley, which maintain their level solely by evaporation, have significantly higher concentrations of deuterated water than do lakes or seawater with at least one outlet.

Heavy water is 10.6% denser than ordinary water, a difference not immediately obvious since they are otherwise physically and chemically similar. The difference can be observed by freezing a sample and dropping it into normal water, where it sinks. With respect to taste and smell, rats given a choice between distilled normal water and heavy water avoided the heavy water, based on smell, and it may be that they detected a different taste as well.

The difference in weight increases the strength of water's hydrogen-oxygen bonds, and this in turn is sufficient to cause differences that are important to some biochemical reactions. The human body naturally contains deuterium equivalent to about five grams of heavy water, which is harmless. When a large fraction of water (> 50%) in higher organisms is replaced by heavy water, the result is cell dysfunction and death.

In normal water, about 1 molecule in 3,200 is HDO (one hydrogen in 6,400 is in the form of D), and heavy water molecules (D$_2$O) only occur in a proportion of about 1 molecule in 41 million (i.e. one in 6,400$^2$). Thus semiheavy water molecules are far more common than "pure" (homoisotopic) heavy water molecules. Deuterium oxide was initially obtained by the electrolysis of ordinary water over a considerable period of time. This method of production requires a large cascade of stills or electrolysis chambers and consumes large amounts of power, so that chemical methods are generally now preferred. The most important chemical method is the Girdler sulfide process.
In this process, demineralised and deaerated water is trickled through a series of perforated (seive) plates in a tower, while hydrogen sulfide gas (BP -60 °C) flows upward through the perforations. Deuterium migration preferentially takes place from the gas to the liquid water. This "enriched" water from the cold tower (maintained at 32 °C) is fed to the hot tower (at 130 °C) where deuterium transfer takes place from the water to the hydrogen sulfide gas. An appropriate "cascade" setup accomplishes enrichment via the reversible reaction:

$$[H_2O + HDS \rightleftharpoons HDO + H_2S]$$

The equilibrium constant, $K$ for, this reaction in terms of the concentrations, can be written as:

$$K = ([HDO][H_2S]) / ([H_2O][HDS])$$

or alternatively:

$$K = ([HDO]/[H_2O]) / ([HDS]/[H_2S])$$

If H and D were the same chemically, the equilibrium constant for the reaction would be equal to unity. However, what is found is that $K$ is not equal to unity, and furthermore it is temperature dependent:

at 25 °C, $K = 2.37$

at 128 °C, $K = 1.84$

From the above information, at 32 °C, the equilibrium favours the concentration of deuterium in water. However, at around 130 °C, the equilibrium is now relatively more favorable to the concentration of deuterium in the hydrogen sulfide. In other words, the concentration of HDO in H$_2$O is greater than the concentration of HDS in H$_2$S but the relative concentration of
HDS in H$_2$S increases with increasing temperature, making it possible to separate D from H.

In the first stage, the gas is enriched from 0.015% deuterium to 0.07%. The second column enriches this to 0.35%, and the third column achieves an enrichment between 10% and 30% deuterium oxide, D$_2$O. Further enrichment to "reactor-grade" heavy water (> 99% D$_2$O) still requires distillation or electrolysis. The production of a single litre of heavy water requires ~340,000 litre of feed water.

In 1934, Norway built the first commercial heavy water plant with a capacity of 12 tonnes per year. From 1940 and throughout World War II, the plant was under German control and the Allies decided to destroy the plant and its heavy water to inhibit German development of nuclear weapons. In late 1942, a planned raid by British airborne troops failed, both gliders crashing. The raiders were killed in the crash or subsequently executed by the Germans. On the night of 27 February 1943 Operation Gunnerside succeeded. Norwegian commandos and local resistance managed to demolish small, but key parts of the electrolytic cells, dumping the accumulated heavy water down the factory drains. Had the German nuclear program followed similar lines of research as the United States Manhattan Project, the heavy water would not have been crucial to obtaining plutonium from a nuclear reactor, but the Germans did not discover the graphite reactor design used by the allies for this purpose.