Groundwater Chemistry

9

9.1 Introduction

If H_2O molecules were the only thing present in groundwater, this chapter could be very short. Thanks to the many other substances within or in contact with groundwater, there is a lot more to talk about. The distribution, reactions, and transport of these other substances make for an interesting and complex topic.

Solutes are other molecules dissolved within the sea of H_2O molecules in the aqueous state. Many solutes occur naturally, such as inorganic ions like Ca^{2+} or SO_4^{2-}. Sometimes high concentrations of naturally occurring solutes render the water unfit for drinking, irrigation, or other uses. Other solutes are chemicals introduced by human activities. Many of these are troublesome contaminants such as heavy metals and organic solvents.

The solid phases that make up the aquifer matrix can react with and dissolve into the groundwater. At the same time, some solids precipitate out of water, a phenomenon that can lead to clogged pipes. Some solids may also exist as tiny particles suspended in the groundwater.

In the unsaturated zone, water is in contact with pore gases and molecules will transfer between the liquid and gas states. This mechanism can be an important way that subsurface contaminants migrate, particularly for volatile organic compounds (VOCs).

When organic liquids like hydrocarbon fuels and solvents are spilled into the subsurface, they dissolve sparingly into water and can persist for a long time as a separate liquid phase. The acronym **NAPL**, for *nonaqueous-phase liquid*, is often used to describe these separate liquid phases.

Chemical reactions can involve substances in the aqueous, gas, solid, or NAPL phases, and some reactions transfer mass from one phase to another. Some reactions occur within the bodies of microorganisms; they are a vital link in the attenuation of certain contaminants. Chemical processes in the groundwater environment are both complex and fascinating. Characterizing and predicting these processes are some of the most challenging problems in groundwater science. Groundwater chemistry is relevant to all users of groundwater resources, whether it be for drinking, irrigation, industrial, or other purposes. Chemistry is also central to understanding the fate of groundwater contamination and how to remediate contamination.

This chapter provides an introduction to aqueous geochemistry as it relates to groundwater. Much more detailed treatment of the subject can be found in aqueous chemistry texts like those of Drever (1988), Pankow (1991), Morel and Hering (1993), Stumm and Morgan (1996), and Langmuir (1997). Domenico and Schwartz (1998) cover aspects of chemistry that are relevant to groundwater. The next chapter introduces groundwater contamination, building on the fundamentals introduced in this chapter.

9.2 Molecular Properties of Water

The geometry of a water molecule is not unlike the face of a famous cartoon mouse (Figure 9.1). The two hydrogen atoms are bonded to the oxygen atom by sharing outer electrons, forming covalent bonds. The angle between the two bonds is about 105°.

Water is a polar molecule because the distribution of electrical charge associated with protons and electrons is asymmetric. The oxygen end of the molecule is somewhat negatively charged, while the hydrogen ends are somewhat positively charged.

The polarity of the water molecule causes electrostatic attraction to other polar molecules and to charged molecules. The hydrogen ends of a water molecule are attracted to the oxygen ends of other water molecules, forming weak bonds known as hydrogen bonds (Figure 9.1). Hydrogen bonding causes water molecules to bond together in clusters within which there is an ephemeral fixed arrangement like in a crystalline solid. These clusters are continually forming and breaking up, existing for only a short slice of time, on the order of 10^{-12} sec (Stumm and Morgan, 1996). These clusters grow as large as 100 water molecules (Snoeyink and Jenkins, 1980).

Several different isotopes of both hydrogen and oxygen occur in natural waters, but the most common isotopes ^{1}H and ^{16}O are far more abundant than all others (see Table 9.13, Section 9.10). The different isotopes of a specific element differ only in the number of neutrons in the atom's nucleus and, of course, their total mass. Because various isotopes of the same element have the same number of electrons, all isotopes behave similarly in chemical reactions.

The difference in mass between different isotopes can lead to different behavior in certain physical processes. For example, water molecules containing the heavier isotopes ^{2}H, ^{17}O, or ^{18}O are less prone to evaporate from liquid water than the common water molecules containing ^{1}H and ^{16}O. This discrepancy leads to near-surface ocean or lake water that is enriched in the heavier isotopes compared to atmospheric water (more about that in Section 9.10).

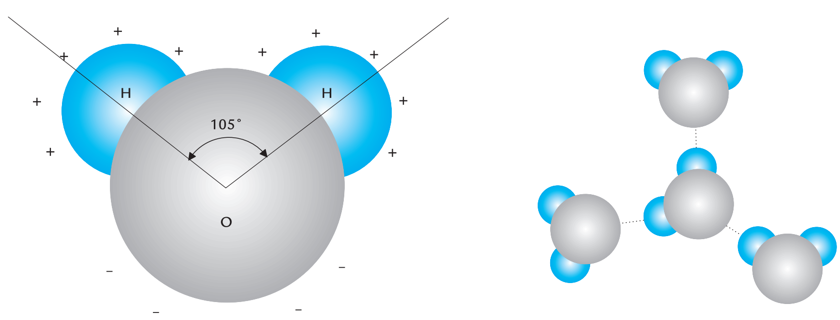

Figure 9.1 Geometry of a water molecule (left) and hydrogen bonding of water molecules (right).