4. CHEMICAL AND PHYSICAL INFORMATION

4.1 CHEMICAL IDENTITY

Information regarding the chemical identity of chlorine is located in Table 4-1. This information includes synonyms, chemical formula and structure, and identification numbers. For the purpose of disambiguation, terms that are commonly used in reference to chlorinated water are defined in Table 4-2.

4.2 PHYSICAL AND CHEMICAL PROPERTIES

Information regarding the physical and chemical properties of chlorine is located in Table 4-3.

Chlorine (Cl_2) is a heavier-than-air, greenish-yellow gas with a pungent, irritating odor (HSDB 2009). The odor threshold for chlorine in air is generally between 0.2 and 0.4 ppm (Amoore and Hautala 1983; The Chlorine Institute 1998). Perceivable sensory irritation occurs at 1.0 ppm in air (EPA 1999). Chlorine is a nonflammable gas; however, it is a very strong oxidizing agent, reacting explosively or forming explosive compounds or mixtures with many common chemicals (O'Neil et al. 2001). Chlorine reacts directly with nearly all of the elements to form chlorides (Lide 2005; O'Neil et al. 2001). Chlorine is stored and transported as a liquid in pressurized containers (EPA 1999). Chlorine is transported as either a liquid or a gas through pipelines within chemical plants or over distances of several kilometers (Schmittinger et al. 2006).

Chlorine hydrolyzes rapidly and almost completely in water to form hydrochloric acid, hypochlorous acid, and hypochlorite as follows:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

The equilibrium constants for these reactions are represented by:

$$K_1 = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} \qquad (1)$$

Table 4-1. Chemical Identity of Chlorine[a]

Characteristic	Information
Chemical name	Chlorine
Synonyms/trade names	Chlorine gas[b], Bertholite, molecular chlorine, chlorine mol, dichlorine
Chemical formula	Cl_2
Chemical structure	Cl—Cl
Identification numbers:	
CAS registry	7782-50-5
NIOSH RTECS	FO2100000[c]
EPA hazardous waste	No data
DOT/UN/NA/IMCO shipping	UN1017; IMO 2.0
HSDB	206
EINECS	231-959-5[c]
NCI	No data

[a] All information obtained from HSDB 2009 except where noted.
[b] EPA 1999
[c] IPCS 1996

CAS = Chemical Abstracts Service; DOT/UN/NA/IMO = Department of Transportation/United Nations/North America/International Maritime Dangerous Goods Code; EINECS = European Inventory of Existing Commercial Chemical Substances; EPA = Environmental Protection Agency; HSDB = Hazardous Substances Data Bank; NCI = National Cancer Institute; NIOSH = National Institute for Occupational Safety and Health; RTECS = Registry of Toxic Effects of Chemical Substances

Table 4-2. Commonly Used Terms Related to Chlorinated Water

Term	Meaning
Chlorinated water	The solution that results when molecular chlorine or a hypochlorite salt is added to water for the purpose of water disinfection. Molecular chlorine reacts rapidly with water under environmental conditions to form hypochlorous acid, hypochlorite, and hydrochloric acid; therefore, chlorinated water does not contain molecular chlorine under normal conditions. Some other substances that are commonly formed in chlorinated water include oxidized inorganics, chloramines, and trihalomethanes.
Free chlorine	The combination of the equilibrium species molecular chlorine, hypochlorous acid, and the hypochlorite ion in chlorinated water. Since molecular chlorine is usually not present in water samples, this term usually refers to the amount of hypochlorous acid and hypochlorite in water.
Combined chlorine	The amount of chloramines (chlorine combined with nitrogen) present in chlorinated water.
Total chlorine	The amount of free chlorine (hypochlorous acid and hypochlorite) plus combined chlorine (chloramines) present in chlorinated water.
Available chlorine	A measure of the oxidizing strength of a solution. It is equal to the amount of molecular chlorine that when added to water would produce a solution with equivalent oxidizing power. It is commonly reported as weight percent.
Residual chlorine	The amount of free chlorine remaining in a chlorinated water sample that has been collected at a point of use. This indicates whether the water has retained its disinfection properties.
Aqueous chlorine	A term that usually has a meaning similar to that of free chlorine. In this sense, “aqueous chlorine” should not be misunderstood as the amount of molecular chlorine in water (aqueous molecular chlorine). The term “aqueous chlorine” is commonly used in reference to a prepared aqueous solution of hypochlorite and hypochlorous acid.

Sources: APHA 1998a; Edstrom Industries 2003; Fukayama et al. 1986; IARC 1991; The Chlorine Institute 2006; Westerhoff et al. 2004; WHO 2007.

Table 4-3. Physical and Chemical Properties of Chlorine[a]

Property	Information
Molecular weight	70.905
Color	Greenish-yellow
Physical state	Gas
Melting point	-101.00 °C
Boiling point	-34.04 °C
Density in air	2.482 (air=1)[b]
Density, as liquid	
20 °C, 6.864 atm	1.4085 g/mL[c]
-35 °C, 0.9949 atm	1.5648 g/mL[c]
Odor	Pungent, irritating
Odor threshold:	
Water	Not applicable[d]
Air	0.2–0.4 ppm[c,e,f]
Solubility:	
Water	14.6 g/L at 0 °C; 7.3 g/L at 20 °C[c,g]
Other solvents	Glacial acetic acid, dimethylformamide, nitrobenzene, phosphoryl chloride, carbon tetrachloride, tetrachloroethane, pentachloroethane, hexachlorobutadiene, and chlorobenzene[h]
Partition coefficients:	
Log K_{ow}	Not applicable
Log K_{oc}	Not applicable
Vapor pressure at 25 °C	5,830 mm Hg
Henry's law constant	1.17×10^{-2} atm-m^3/mol[i]
Autoignition temperature	Not applicable
Flashpoint	Not applicable
Reactivity	Strong oxidizer; reacts explosively with many materials
Conversion factors	1 ppm=2.9 mg/m^3; 1 mg/m^3=0.344 ppm[c]

[a] All information obtained from HSDB 2009, except where noted.
[b] O'Neil et al. 2001
[c] EPA 1999
[d] Amoore and Hautala (1983) reported an odor threshold of 0.002 ppm for chlorine in water; however, these authors state that this solution lacks enough persistence for this value to be used for reference purposes.
[e] Amoore and Hautala 1983
[f] CI 1998
[g] EPA 1994b
[h] Schmittinger et al. 1996
[i] Staudinger and Roberts 1996

$$K_2 = \frac{[H^+][OCl^-]}{[HOCl]} \qquad (2)$$

The relative percentage of Cl_2, HOCl, and OCl^- at some fixed concentration of Cl^- can be expressed as:

$$\%Cl_2 = \frac{[Cl_2]}{[Cl_2]+[HOCl]+[OCl^-]} \qquad (3)$$

$$\%HOCl = \frac{[HOCl]}{[Cl_2]+[HOCl]+[OCl^-]} \qquad (4)$$

$$\%OCl^- = \frac{[OCl^-]}{[Cl_2]+[HOCl]+[OCl^-]} \qquad (5)$$

Using the expressions for the equilibrium constants in Equations 1 and 2 and the relationship that pH is equivalent to the negative logarithm of the hydronium ion concentration, Equations 3–5 can be re-written as:

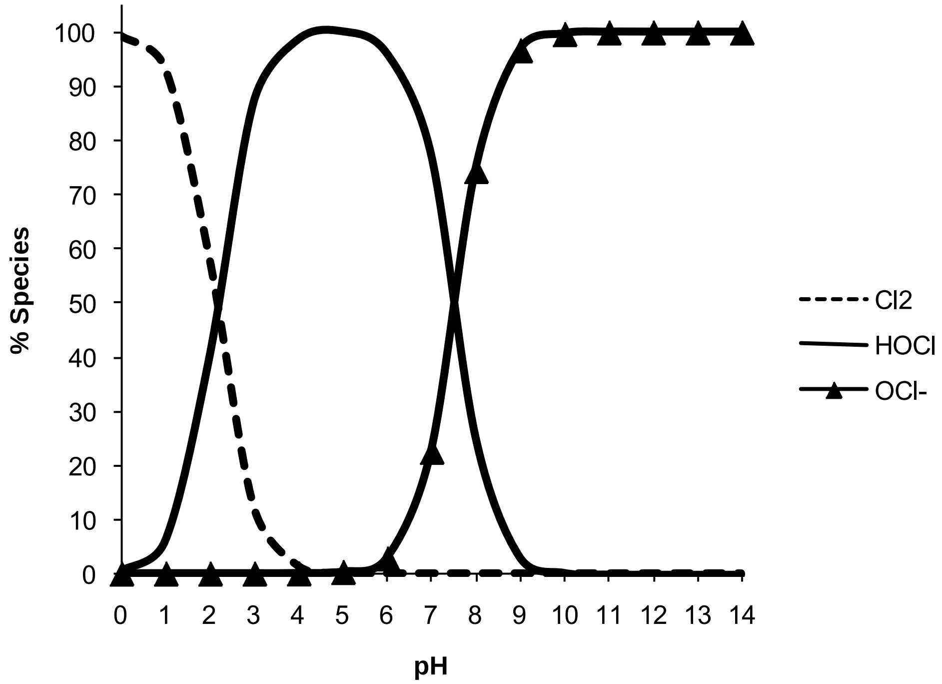
$$\%Cl_2 = \frac{1}{1+\frac{K_1}{[Cl^-]}10^{pH}+\frac{K_1K_2}{[Cl^-]}10^{2pH}} \qquad (6)$$

$$\%HOCl = \frac{1}{1+\frac{[Cl^-]}{K_1 10^{pH}}+K_2 10^{pH}} \qquad (7)$$

$$\%OCl^- = \frac{1}{1+\frac{[Cl^-]}{K_1K_2 10^{2pH}}+\frac{1}{K_2 10^{pH}}} \qquad (8)$$

Figure 4-1 illustrates the speciation as a function of pH using values for $K_1 = 3.9\text{x}10^{-4}$ M^2 (Cotton et al. 1999; Farr et al. 2003) and $K_2 = 2.9\text{x}10^{-8}$ M (Farr et al. 2003) at 25 °C. This figure shows the

Figure 4-1. Speciation of Cl_2, HOCl, and OCl^- as a Function of pH



pH-dependant relationship between molecular chlorine, hypochlorous acid, and hypochlorite in aqueous solution. Sodium hypochlorite bleach solutions typically have a pH of 11–13 (The Chlorine Institute 2006). As illustrated in Figure 4-1, the addition of acid to a hypochlorite solution (e.g., mixing of sodium hypochlorite bleach with acid drain cleaner) can drive the pH low enough to result in the release of dangerous amounts of molecular chlorine gas.