Chapter 15
Water

15.1 Introduction

In recent years, strenuous efforts have been made to conserve and recycle resources. Of major concern has been *water* due to its rising consumption and resultant shortage. Any discussion of water must include its domestic and industrial use. The treatment of waste sewage is the concern of sanitation engineers and will not be considered here.

Some selected basic properties of water are given in Table 15.1. The unique characteristics of water, although not obvious, will become apparent as we learn more about it. The three-dimensional phase diagram for water, up to the pressure of 10,000 atm and for the temperature range of $-50°C$ to $+ 50°C$, is shown in Fig. 15.1. The density of ice (ice I) is less than that of water up to about 2,200 atm. Above this pressure, ice exists in various different crystalline modifications. The two-dimensional phase diagram for water is shown in Fig. 15.2, where the triple point, 0.0100°C, consists of solid ice, water, and water vapor at 4.579 torr in equilibrium. Also shown is the critical point above which liquid water cannot exist in the liquid state. The negative slope of the *P*-*T* line is due to the difference in molar volumes of liquid and solid, that is, $(V_t - V_s) < 0$, and because

$$dP/dT = dH_{fus}(V_t - V_s/T) \tag{15.1}$$

This situation exists for only four known substances, water, bismuth, iron, and gallium, where the solid floats on the liquid at the melting point. Water is unique, however, since its maximum density is not at 0°C but at 4°C. This is illustrated in Fig. 15.3 where the partial structure of dimers and trimers due to hydrogen bond formation allows for a more structured arrangement of the water clusters. This structure is disrupted as salt is added, as shown in Fig. 15.4, where the maximum density drops from 4°C to $-1.33°C$ at 24.7 ppt (parts per 1,000). At higher salt concentrations, the density of water increases with decrease in temperature. Ice formed from saltwater is normally free of salt and has the normal density of ice, that is, 0.9170 g/mL.

Water is essential to humans. The average consumption per person is 2 L/day. The average household uses about 200 L/day. Water is also necessary for many industries, for example, 250 L is required for the manufacture of 1 kg of steel and 1 kg of aluminum requires about 1,300 L of water. Ten liters of water is needed for the production of each liter of gasoline, 250 tonnes for each tonne of paper, and 450 L to grow enough wheat to bake a loaf of bread, grow 1 kg of potatoes, or produce one weekend newspaper.

The amount of water on the earth's surface is about 1.4×10^9 km^3 of which only 3% is non-ocean water and of which two-thirds is in the form of ice on the polar ice caps. The remaining 1% is surface and underground water in a relative ratio of about 1:3. These ratios are changing slowly due to the

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Table 15.1 Selected properties of water

Molar mass (g/mol)	18.0153	
Melting point (°C)	0.0000	
Boiling point (°C)	100.000	
Triple point (°C)	0.0100	
Density liquid at 25°C (g/mL)	0.997044	
Density liquid at 0°C (g/mL)	0.999841	
Density solid at 0°C (g/mL)	0.9170	
δH°_f (liquid) (kJ/mol)	−285.8	Standard enthalpy of formation
δH°_f (gas) (kJ/mol)	−241.8	Standard enthalpy of formation
δG°_f (liquid)	−237.2	Standard free energy of formation
δG°_f (gas) (kJ/mol)	−228.6	Standard free energy of formation
S° (liquid) (J/mol K)	69.9	Standard entropy
S° (gas) (J/mol K)	188.7	Standard entropy
δH_{fus} (kJ/mol)	5.98	Enthalpy of fusion
δH_{vap} (kJ/mol)	40.5	Enthalpy of vaporization
Heat capacity (solid) (J/mol K)	37.6	
Heat capacity (liquid) (J/mol K)	75.2	
Thermal conductivity (solid) (J/s m K)	2.1	
Thermal conductivity (liquid) (J/s m K)	0.58	
Dipole-moment (Debye)	1.84	
H—O—H angle	104°	
Bond length, H—O (pm)	96	
γSurface tension (mJ/m^2) at 25°C	72	
h_iViscosity (poise, 10^{-1} kg m^{-1} s^{-1}) 25°C	0.01	
T_c, Critical temperature (°C)	347.15	
P_c, Critical pressure (atm)	218.3	
V_c, Critical volume (cm^3/mol)	59.1	
E (H—O) (kJ/mol)	464	Bond energy
D (HO—H) (kJ/mol)	498.7	Bond dissociation energy
D (O—H) (kJ/mol)	428.0	Bond dissociation energy
K_{ion} at 25 °C	1.002×10^{-14}	Ionization constant
pK_w at 25 °C	13.999	
Vapor pressure		
T(°C) 0 10 20 25	50 75	90 100
P(torr) 4.6 9.2 17.5 23.8	92.5 289.1	525.8 760

evidence showing that the north polar ice is receding. It will result in the rise of sea level and the possible flooding of costal land and cities.

Seawater consists of 3.5% by weight of dissolved solids, mostly NaCl with Mg^{2+}, Ca^{2+}, K^+, and SO_4^{2-} as the main ions with many more trace components in the ig/mL and pg/mL range. For example, uranium is present in seawater at around 3 pg/mL, and gold is about 1,000 times less concentrated (i.e., 3 pg/L). Distribution of water on the earth's surface is shown in Table 15.2. Water quality (as determined by standard chemical analysis) of the drinking water from some Canadian cities and some commercially available spring waters is listed in Table 15.3. Also included are the guidelines recommended by the World Health Organization (WHO). Table 15.3 lists the WHO guidelines for the limits of organic substances which are considered a health hazard in potable water. These substances are seldom analyzed, but readily show their presence by ultraviolet absorption spectrophotometry.

Attempts to alleviate the water shortage which exists in many parts of the world have included extensive efforts to desalinate seawater. This continuing effort will be discussed later.

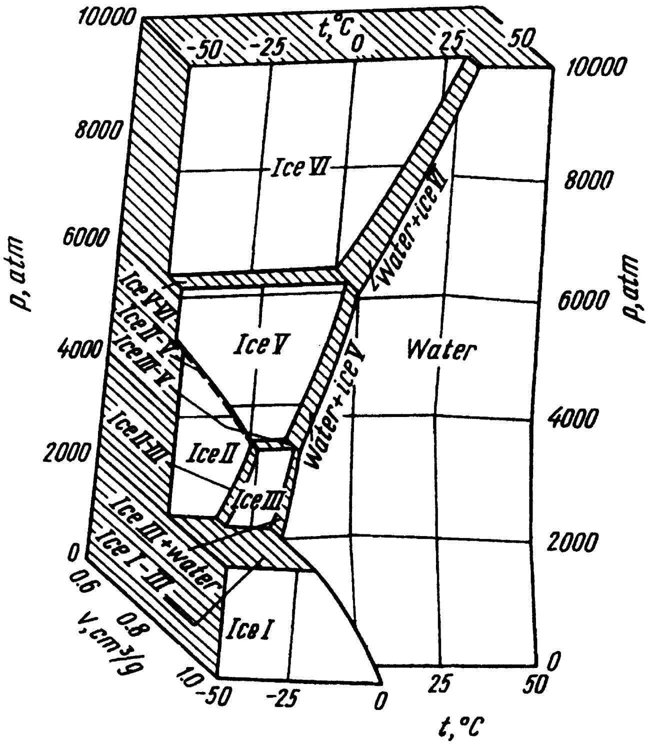


Fig. 15.1 The 3-D phase diagram of water showing the various modifications of ice (Ice IX is not shown in the diagram)

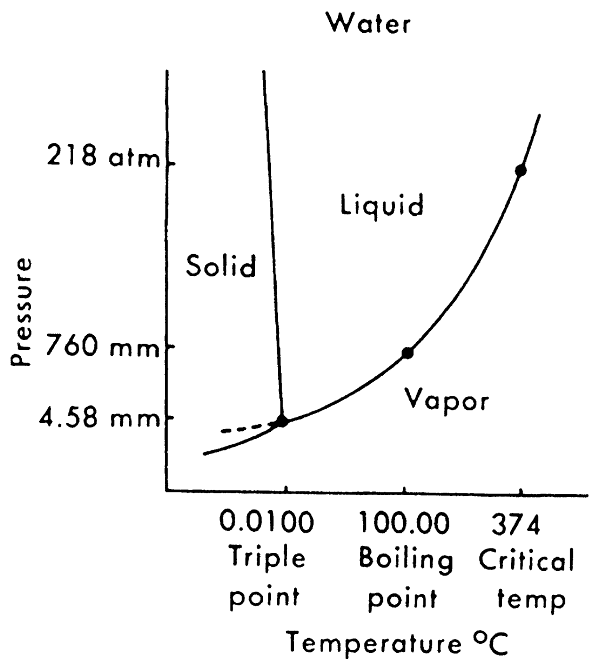


Fig. 15.2 The 2-D phase diagram of water showing the triple point, critical temperature, and critical pressure

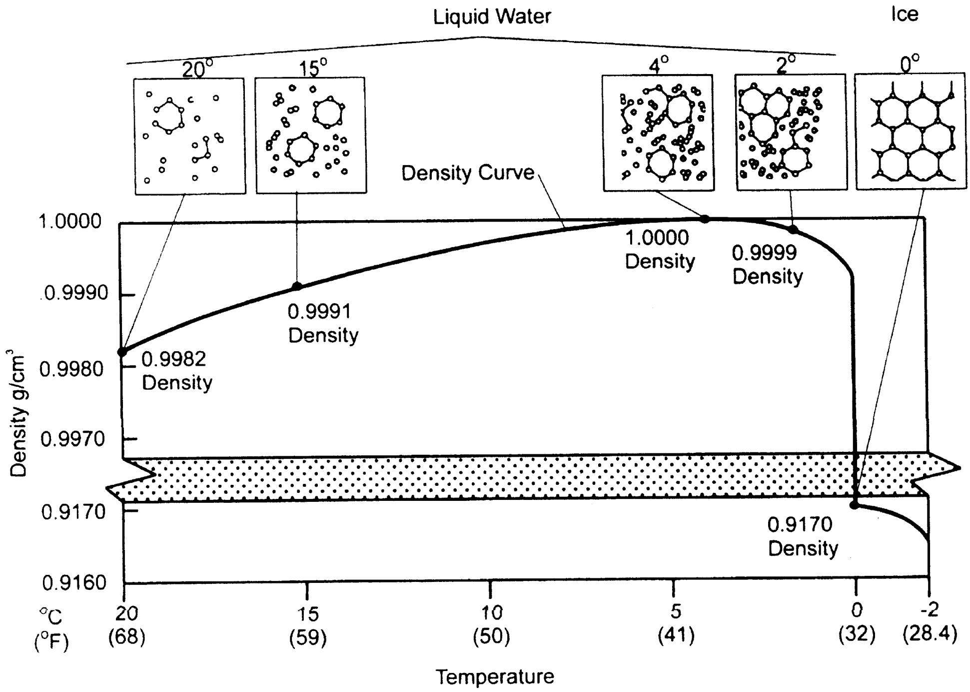


Fig. 15.3 A pictorial description of the changes in water structure near the position of maximum density, and as water changes to ice, it shows the formation of ice clusters in freshwater. The density of freshwater ranges from 0.9982 g/cm^3 at 20°C to a maximum of 1.000 g/cm^3 at 4 °C. However, the density of ice (*solid water*) is only 0.9170 g/cm^3, so it floats on water

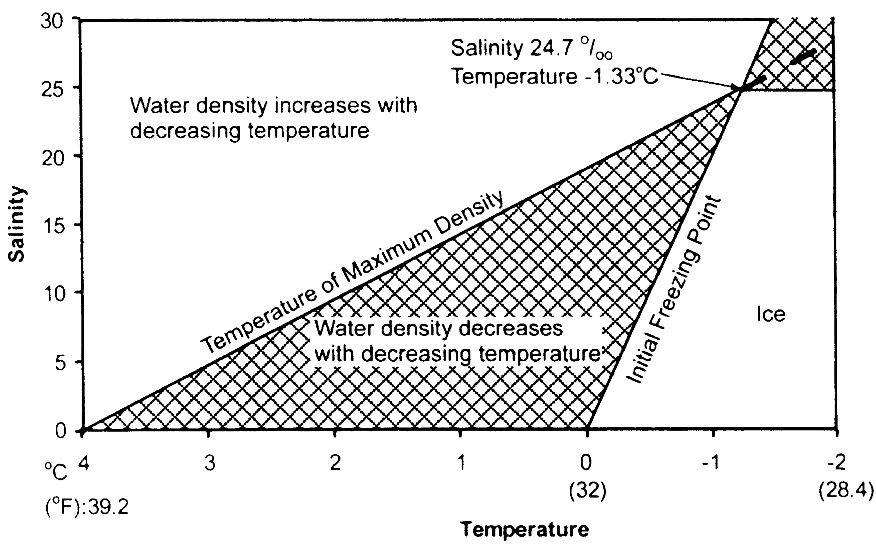


Fig. 15.4 Freezing point and temperature of maximum density as a function of salinity (grams of salt per 1,000 g of solution)

One elaborate scheme, proposed by Prince Mohamed Al Faesal of Saudi Arabia, involves the towing of icebergs, which are essentially salt free, from the Antarctic to desert countries. It is calculated that at a speed of 3 knots, the trip could take over 100 days and that a 1-km-long iceberg would melt before reaching the Gulf of Arabia. Hence, it was proposed to insulate the iceberg to

Table 15.2 Approximate water distribution on the earth's surface

Source	(%)
Oceans	96.1
Ice and snow	2.2
Underground	1.2
Surface and soil	0.4
Atmosphere	0.001
Living species	0.00003
Total $= 1.36 \times 10^9$ km^3	*100*

Table 15.3 WHO guidelines for organic constituents in drinking water (1984)

Constituent	Concentration (μg/L)
Aldrin and dieldrin	0.03
Benzene	10
Benzo(a)pyrene	0.01
Carbon tetrachloride	3
Chlordane	0.3
Tetrachloroethane	10
Trichloroethene	30
Chloroform	30
1,2-Dichloroethane	10
1,1-Dichloroethane	0.3
2,4-D	100
Heptachlor and heptachlor epoxide	0.1
Hexachlorobenzene	0.01
Lindane	3
Methoxychlor	30
Pentachlorophenol	10
2,4,6-Trichlorophenol	10

reduce its melting rate. The ice could also be used for air conditioning while being converted into potable water. The estimated cost of the water was determined to be about $0.06 per 1,000 US gal.

Another recent scheme involved the transportation of water by sea from areas of plentiful supply in floating inflatable bags—called the *Medusa bag*—to areas where water is in short supply. This is considered feasible because freshwater is less dense than seawater and will float on the ocean surface.

15.2 Natural Water

The main source of domestic water is *natural water* which includes lakes, rivers, and wells. It is characterized by a variety of measurable quantities which include color, turbidity, odor, bacteria, suspended solids, total solids, pH, conductivity, and most importantly, hardness.

15.2.1 Turbidity

Suspended solids and colloids cause water to be turbid. Various turbidity scales have been established for the determination of the relative *turbidity* of a water sample. Active carbon filtration can often clarify water by adsorbing colored components and removing colloids.

15.2.2 Color

The presence of dissolved organic substances in water gives rise to coloration. The *color* of water can be determined by various methods that either involve a comparison with standards which are either colored glass or standard solutions of a blend of K_2PtCl_6 and $CoCl_2$, or by the more comprehensive approach, namely the spectrophotometric method, where the transmission of visible light is determined as a function of the wavelength of light.

The color value of water depends on pH and usually increases as the pH increases. Hence, the specification of color must also include the pH value of the water.

15.2.3 Odor and Taste

The presence of both organic and inorganic compounds in water contributes to the "chemical" senses—*odor* and *taste*. Pure distilled water is free of contaminants and has neither odor nor taste. The odor and taste of water can be removed by passing water through a column of activated carbon. Good-grade drinking water is free of odor and toxic substances and has a pleasant taste.

Aeration also improves odor and taste and is often the standard treatment during the conversion of natural waters to potable grade. This full treatment involves filtering the intake water to remove debris, fish, and other large items. The water is then treated with trivalent cations such as alum [$KAl(SO_4)_2$•$12H_2O$] and ferric chloride ($FeCl_3$) that hydrolyze to amorphous, gelatinous precipitates, $Al(OH)_3$ and $Fe(OH)_3$, respectively, and as the floe settles by gravity, it clarifies the water by trapping and adsorbing the suspended impurities. Aeration is used to improve the color, odor, and taste of water. The soluble organic compounds and salts are adsorbed on activated carbon followed by disinfection by the addition of chlorine.

15.3 Water Sterilization

15.3.1 Chlorine

Water for drinking purposes—potable water—is treated to make it acceptable and free of harmful bacteria. This is most often accomplished by adding *chlorine* to the water which forms the strong oxidizing hypochlorous acid, HOCl:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{15.2}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \tag{15.3}$$

Depending on pH and products formed, the effective residual concentration of chlorine [free available chlorine (FAC)] HOCl or "OCl" is 0.1–0.2 mg/L. Higher concentrations tend to give water a definite taste.

A more persistent source of the hypochlorite ion is the chloramines (made from the reaction of chlorine with ammonia at pH 4.5–8.5):

$$Cl_2 + NH_3 \rightleftharpoons NH_2Cl + HCl \tag{15.4}$$

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \tag{15.5}$$

Dichloramine, pH 4.5, and trichloramine, pH 4.4, are formed by successive additions of Cl_2 or HOCl to the monochloramine. Chloramines impart a green color to water. As the hypochlorite ion is consumed by oxidizing the contaminants, the chloramines supply more HOCl and so maintain a "safe" level of primary disinfectant. Excess chlorine is removed by reaction with sodium bisulfate:

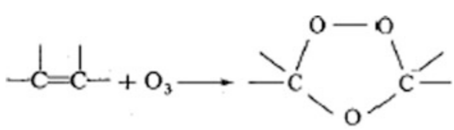
$$NaHSO_3 + H_2O + Cl_2 \rightarrow NaCl + H_2SO_4 + HCl \tag{15.6}$$

The chlorine demand is the difference between the chlorine added and the residual concentration after a designated reaction time of approximately 10 min. Total residual chlorine is determined by the oxidation of *N*,*N*-diethyl-*p*-phenylenediamine (DPD) to produce a red-colored product. Addition of iodine then catalyzes further reaction with chloramines, and it is possible to obtain concentration values for all chloramines and free chlorine.

The extensive use of chlorine to purify water has recently been shown to result in the formation of chlorinated hydrocarbons. Low molecular weight compounds, such as the haloforms (HCX_3), also called trihalomethanes (THM), are volatile and have been shown to be carcinogenic. They have been detected in drinking water and in the air of enclosed swimming pools. Thus, several alternate disinfectants (such as ozone, chlorine dioxide, UV, and ferrates) have been considered as alternates to chlorine. Of these, the use of ozone has been most developed.

15.3.2 Ozone

Ozone is a triatomic molecule of oxygen, O_3, with a triangular structure where the O—O—O angle is 116° 49′. It has been used as a water disinfectant since 1903, and water treatment is the single major use of ozone. Next to fluorine (F_2), it is the most powerful oxidizing agent available. Its widespread use is due to its ability to add readily across a carbon–carbon double bond to form an ozonide

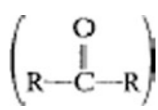


ozonide

(15.7)

which subsequently decomposes to form aldehydes, RCHO, and ketones.

Ozone also decomposes to form an oxygen atom that is also a powerful oxidizing agent. Ozone is prepared either by the photodissociation of oxygen (O_2)



(15.8)

$$\begin{aligned} O_2 + h\upsilon &\xrightarrow{\lambda < 200\,\mathrm{nm}} 2O \\ O + O_2 &\longrightarrow O_3 \end{aligned} \tag{15.9}$$

or by a high-voltage ac electrical (silent) discharge through oxygen (or air). A typical ozone generator is shown in Fig. 15.5.

A mixture of ozone and air can be bubbled through water to oxidize impurities. Ozone is toxic and can be detected by its odor at about 0.01 ppm, whereas its TLV is 0.1 ppm.

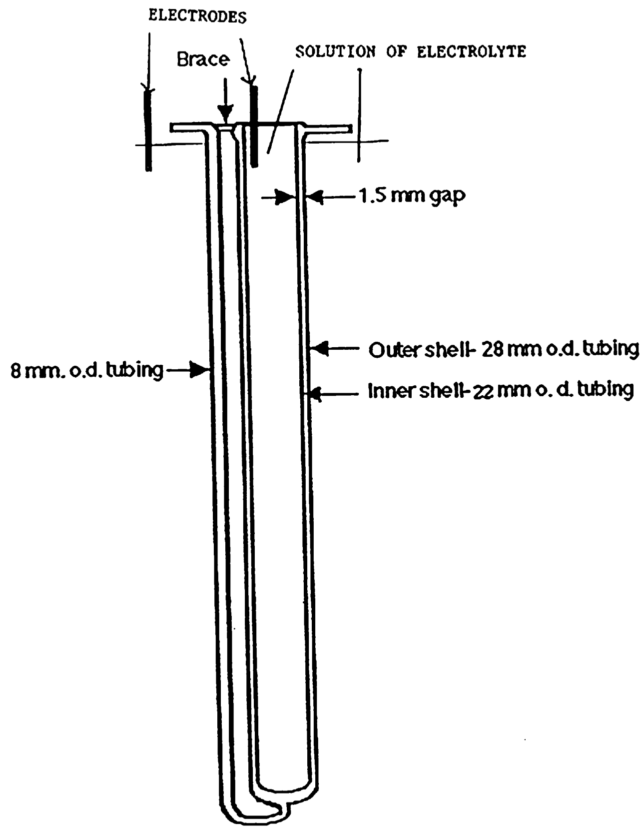


Fig. 15.5 Silent discharge reactor tube for ozone production. The tube is rilled with electrolyte and placed in a container full of electrolyte solution which holds the high-voltage ac electrodes. The electrolyte is usually copper sulfate or sodium sulfate in water. The electrodes are usually copper

Unlike chlorine, ozone does not produce known carcinogens as a byproduct of its water treatment and, therefore, is gaining increased use for domestic as well as industrial water supplies. In North America, chlorination must follow ozonation in public water supply because ozone decomposes rapidly, and a chlorine residual may be carried throughout a distribution system. Chloramines are often used.

15.4 Infectious Agents

The final criterion of satisfactory sterilization of domestic water is the reduction in bacterial concentration to very low values. Bacteriological examination of drinking water uses the coliform bacteria (*Escherichia coli*—often referred to as *E. coli*) as an indication of the purity of the water since these bacteria are the normal inhabitant of the intestinal tract and constitute about 30% of the dry weight of adult human feces. Water suitable for human consumption should contain less than one viable coliform per 100 mL.

Three different types of standard tests are used:

1. *Multiple-type fermentation method.* The various aliquots of samples are incubated for 48 h at 35°C in a culture medium. The absence of gas formation indicates a negative test for coliform.

2. *Membrane filter technique*. Water is filtered through a 0.45-μm sterile filter which is then placed in a culture medium and incubated at 35°C for 24 h. The growth of visible colonies on the filter indicates the number of bacteria present.
3. *Standard plate count method*. Various diluted volumes of the sample are added to a solid agar culture medium and incubated at 35°C for 72 h. The colonies are counted and recorded as the number per milliliter.

Common bacterial concentration is designated as the "most probable number" (MPN) per 100 mL and represents a statistical interpretation of the results of replicate analysis.

Prior to the 1950s, most houses and buildings used galvanized iron pipes to distribute water. However, these pipes corroded and usually started leaking after about 25 years. Copper has since replaced iron, and because of the solder joints which contain lead, copper is being replaced by plastic for cold-water systems and CPVC and polybutylene are commonly used for both hot- and cold-water lines. There are, however, a large number of older houses which still have lead water pipes or lead connectors from the city water line. This metal is appreciably soluble in water containing carbon dioxide or organic acids. Chloride of lead ($PbCl_2$) is also soluble to a considerable extent. Cases of chronic lead poisoning have been observed due in some instances to the habitual use of water that remained in the lead pipes overnight. The fall of ancient Rome is attributed by some scholars to the use of lead casks and vessels to store wine.

It was shown in the 1930s that fluoride in natural waters in concentrations greater than 4 ppm caused a brownish discoloration or mottling of tooth enamel. Prior to World War II, it was demonstrated that such teeth were free from cavities. In 1945, fluoride was, for the first time, added to the public water supply in Grand Rapids, Michigan. Since then it has been confirmed throughout the world that fluoride added to drinking water reduces cavities in tooth enamel. Fluoride is now usually added to domestic water supplies as Na_2SiF_6 to bring the F^- level to about 1 g/mL. Though fluoride in high concentrations is harmful, the benefits of reduced dental cavities offset the potential hazards. However, many people disagree with this and often resort to drinking only distilled water.

15.5 Water Quality: Hardness

The quality of water varies considerably from one city to another and from one natural source to another. The results of analysis of several water supplies are given in Table 15.3. The water for three Canadian cities and some common spring bottled waters are compared with freshly fallen snow. Specific conductivity is a rough measure of the total ion concentration in the sample. Metallic ions are determined simultaneously by their emission spectra in a plasma or flame. Anions usually require special colorimetric methods. Spring waters listed in Table 15.3 show differences which do not truly demonstrate the organic content of the water. Only by a measure of the UV transmission through at least a 10 cm path length of water over the wavelength range of 200–360 nm is it possible to show which of the waters is the cleanest. Surprisingly, the fresh fallen snow is not the purest water.

One of the most important characteristics of domestic and industrial water, especially in boiler water systems, is a measure of its *hardness*. The hardness of water is due to the bicarbonate ion (HCO_3^-) which, in the presence of calcium and magnesium ions (Ca^{2+}, Mg^{2+}), will form insoluble carbonates when heated:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CO_2 + H_2O \tag{15.10}$$

$$Mg^{2+} + 2HCO_3 \rightarrow MgCO_3\downarrow + CO_2 + H_2O \tag{15.11}$$

Hardness due to carbonate is formed when carbon dioxide (CO_2) in air is dissolved in water which is in contact with calcium carbonate ($CaCO_3$ or limestone):

$$CaCO_3 \downarrow + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{-} \tag{15.12}$$

This reaction is reversed at high temperatures, precipitating the $CaCO_3$, which forms as scale on the surfaces of heaters or other hot surfaces.

Hardness of a water supply is measured in terms of the equivalent amount of $CaCO_3$ that would precipitate. Thus, 40 mg/L of Ca^{2+} (1 mM) would form 100 mg/L of $CaCO_3$ (1 mM). Similarly, 24.3 mg/L of Mg^{2+} (1 mM) would also produce 1 mM equivalent of $MgCO_3$, and its hardness (in mg/L) would also be 100.

Soap consists of the sodium salt of a fatty acid that ionizes in water:

$$RCOONa \rightarrow RCOO^{-} + Na^{+} \tag{15.13}$$

The cleaning agent is the fatty acid anion $RCOO^{-}$ which is precipitated by divalent or trivalent metal ions such as Ca^{2+}, Mg^{2+}, and Al^{3+}:

$$2RCOO^{-} + Ca^{2+} \rightarrow (RCOO)_2Ca \downarrow \tag{15.14}$$

The presence of calcium or magnesium bicarbonate in water is called temporary hardness and requires the use of excess soap to precipitate the free Ca^{2+} and Mg^{2+} before the soap can work. Detergents are synthetic ionic compounds, for example, sodium salts of sulfonic acids,

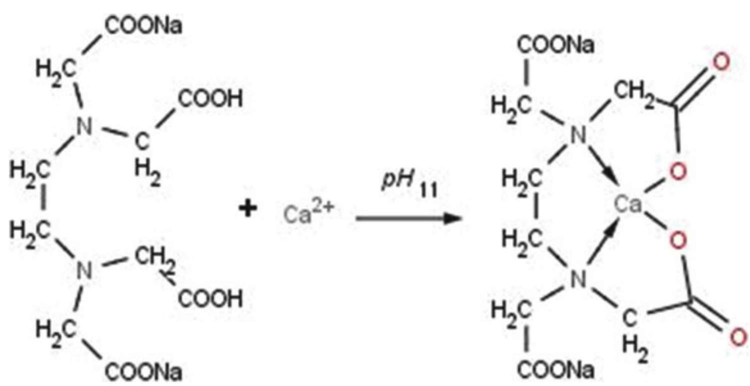
$$(C_nH_{2n+1})-C_6H_5-SO_3^{-}+Na^{+}$$

where $n = 10$–20.

The detergent anion does not form an insoluble salt with divalent or trivalent cation, and hence, it can function in hard water almost as efficiently as in soft water, if in very hard water, the Ca^{2+} and Mg^{2+} are complexed by "builders" such as sodium pyrophosphate ($Na_4P_2O_7$) or sodium tripolyphosphate ($Na_5P_3O_{10}$). The extensive use of phosphates with detergents has resulted in contamination of rivers and lakes since the detergents are not as readily biodegradable as fatty acids, though recent modification has improved this. Phosphates which are released supply a required nutrient to aquatic plants, namely, algae, which can overrun a lake with algal bloom (eutrophication), depriving the water of oxygen needed by living organisms. Lakes can die if corrective measures are not instituted. Thus, nonphosphate detergents have been developed which now include "builders," such as sodium citrate, to complex the calcium and magnesium ions in hard water.

Hardness is determined by an analysis of the Ca^{2+} and Mg^{2+} ions in solution, together with the remaining multivalent ions. Titration can be easily performed using a chelating reagent ethylenediaminetetraacetic acid (EDTA).

EDTA combines with many multivalent cations such as Ca^{2+} to form an octahedrally coordinated chelate complex CaH_2EDTA.



15.6 Water Softening

Hard water can be softened by several methods which vary in efficiency and cost. Distillation will result in water free of dissolved salts and nonvolatile organic substances. This can be carried out using solar energy, and many devices have been described whereby seawater can be converted into potable drinking water, usually on a small scale.

Water frozen slowly will be free of dissolved organic and inorganic compounds. The freeze-thaw cycle is used to purify semiconductors by the process called *zone refining*. Fog and dew have also been used as sources of freshwater.

The removal of the Ca/Mg hardness can be effected by the lime process. In this process, lime (as CaO or $Ca(OH)_2$) is reacted with $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$ to form $CaCO_3$ and $Mg(OH)_2$, respectively:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O \tag{15.15}$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + Ca(HCO_3)_2 \tag{15.16}$$

Lime to be added is calculated from the measured Ca/Mg hardness and adjusted to a pH of 9–9.5 for calcium removal, but a pH of about 12 is needed to remove most of the Mg^{2+}.

The $CaCO_3$ can be used to regenerate the lime by the reaction

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \downarrow \tag{15.17}$$

Lime treatment does not remove all of the hardness. However, should complete removal be required, then the final treatment involves ion-exchange resins or distillation.

15.6.1 Ion Exchange

Naturally occurring minerals, such as *zeolites* or *permulites*, are sodium aluminum silicates ($NaAlSiO_4$) which can exchange sodium for calcium or magnesium:

$$2NaAlSiO_4 + Ca^{2+} \rightarrow 2Na^+ + Ca(AlSiO_4) \tag{15.18}$$

Zeolite can be regenerated by the addition of salt (NaCl) which reverses reaction (15.18).

More efficient ion exchangers such as synthetic polymers of substituted polystyrene are referred to as *ion-exchange* resins. These are either cation or anion exchangers and when mixed together in a single bed, will deionize water to a distilled water grade if the cation exchanger is initially in the protonated or acidic form (H^+) and the anion exchanger is in the basic or hydroxide (OH^-) form. If the cation exchanger is in the sodium form (R.Na), then the resin will exchange Ca^{2+} and Mg^{2+} for Na^+:

$$2R.Na + Ca^{2+} \rightarrow (R)_2Ca + 2Na^+ \tag{15.19}$$

Regeneration of the single-bed ion exchangers is the reverse reaction, that is, adding a solution of NaCl for reactions (15.17) and (15.18). In the case of the complete deionization process of water, acid (HCl) must be used to regenerate the cation-exchange resin, and base (NaOH) is used to regenerate the anion-exchange resin.

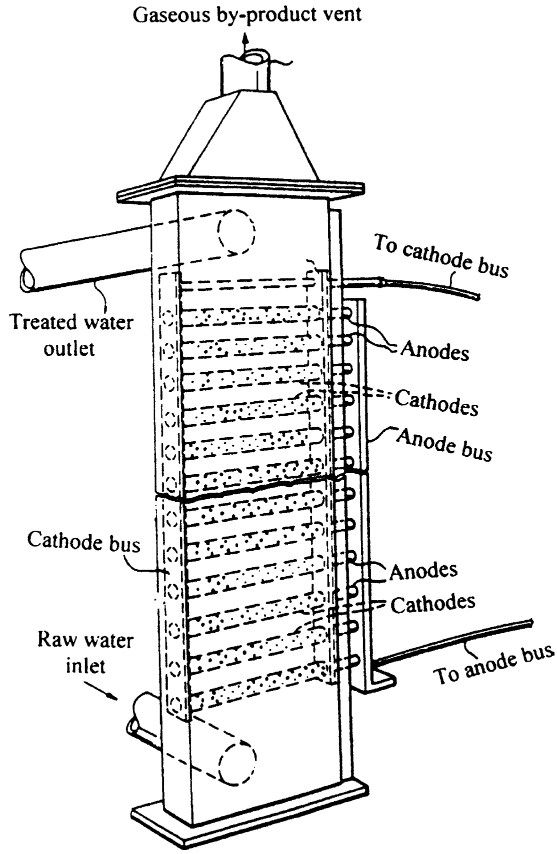


Fig. 15.6 Electrolysis cell used in the electrocoagulation process of converting raw water into potable water

15.6.2 Reverse Osmosis

Another popular method which gives a high-quality water is *reverse osmosis* (RO), often called *ultrafiltration* or *hyperfiltration.* Though often considered too expensive for industrial use, RO has found extensive applications in domestic water supplies. The production of highly efficient osmotic membranes has made RO competitive with distillation for the production of salt-free water. RO does not, however, remove volatile organic compounds (VOC) from the water supply. Treatment with granulated activated carbon (GAC) can be very effective for this purpose (see Chap. 16 and Appendix C).

15.6.3 Electrocoagulation

Recently, it has been reported that a simple patented process can convert raw water into potable water. Raw water is passed through a specially designed electrolysis cell shown in Fig. 15.6. Anodes and iron rods are centered in perforated cylindrical stainless steel cathodes with a spacing gap of about 1.5 mm between anode and cathode. The DC voltage across the electrodes is 3 V, drawing a current of about 0.2 A, producing an electrical field of up to 2,000 V/m. Raw water flows upward carrying the evolved gases, namely, oxygen and hydrogen (though ozone has also been reported), to an exhaust vent. Single units have 10–20 cells in parallel.

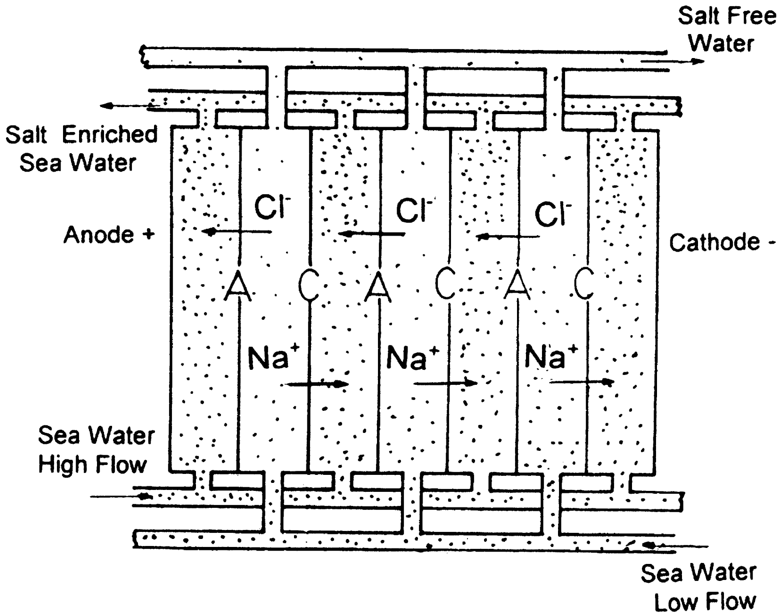


Fig. 15.7 Schematic representation of the desalination of water by electrodialysis. "A" refers to the anion-exchange membrane, and "C" refers to the cation-exchange membrane. The applied voltage attracts the ions from the low-flow water stream into the high-flow wastewater

This process has been used to prepare potable water from natural, industrial-contaminated, and sewage-effluent water. Bacteria such as *E. coli* and Coliform are removed, organic material is oxidized, and heavy metals are plated out or precipitated. The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are reduced, as well as the hardness of the water. The biochemical oxygen demand (BOD) is defined as the amount of oxygen needed by bacteria in aerobic stabilization of organic matter in water. Chemical oxygen demand (COD) is the oxygen needed to completely oxidize the organic matter in water.

How does the system work? It has been proposed that the highly reactive hydroxyl (OH) radical is responsible for the strong oxidizing power. The OH radical could be formed by Fenton's reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \ OH^{-} + {}^{*}OH \tag{15.20}$$

Since O_3 may be formed, it is likely that hydrogen peroxide may also be produced. Fe^{2+} is readily formed from the iron anode.

Another possible process which may be occurring depends on the presence of chloride (Cl^-) ions in the treated water. Chloride could be oxidized to chlorine (Cl_2), which can oxidize the organic matter and kill the pathogenic bacteria. In either case, the electrolysis relies on reactants which are formed during the electrolysis. The simplicity of this process and its reported effectiveness make it an attractive method of recycling water.

15.6.4 Electrodialysis

An electrode potential can direct the motion of ions that depends on the polarity of the voltage and the sign of the charge of the ions. This is illustrated in Fig. 15.7 where the flow of cations is directed through cation-exchange membranes (C), moving toward the negative terminal, and anions will move in the opposite direction through the anion-exchange membrane (A), depleting the solution of ions. The alternate channels, however, become enriched in salt. The flowing current is an indication of the desalination process. When freshwater is alternated with saline water and separated by the anion- and cation-exchange membranes, the movement of ions from the saline to the freshwater channels will result in a current flow and represent a means of generating electrical energy. This is called *reverse electrodialysis.*

Some water-softening (conditioning) units which are sold for domestic use are advertized as "no saltwater conditioners." These units are reported to remove $CaCO_3$ from hard water by using a catalyst, which by epitaxial nucleation, and the reduction of pressure by virtue of a change in water velocity, converts the $Ca(HCO_3)_2$ into $CaCO_3$ and CO_2. These units are very attractive and are advertised to work with detergents but are not intended for use with soap. This can be interpreted to mean that the calcium ions are not removed from the water system and that a precipitate will form from the calcium salt of the fatty acid from the soap (Eq. 15.14).

15.7 Boiler Scale

There are several types of scales that deposit on the hot surfaces in a boiler. The most common is calcium carbonate, which is formed from the hardness of water. Scale is also formed from the deposition of insoluble salts such as calcium sulfate, calcium phosphate, or insoluble silicates. The relation used to calculate the influence of scale on the temperature drop across a boiler tube is

$$\Delta T = QL/K \tag{15.21}$$

where Q is the heat transferred in W cm^{-2}, L is the thickness of the scale in cm and K is the thermal conductivity in Wcm^{-1} K^{-1}, and ΔT is the temperature drop across the pipe in K or °C.

The thermal conductivity of scale such as $CaCO_3$ is approximately 0.03 W cm^{-1} K^{-1} and that of $CaSO_4$ is around 0.003 W cm^{-1} K^{-1}. Production of steam at 600 psi (40 atm) in a 4-cm OD tube of SA 210 carbon steel 3.4 mm thick *(*$K = 0.41$ W/cm K) that requires a heat flux of 40 W/m^2 has a temperature gradient across the steel tube (32 K) and a water boundary film of about 2 mm (40 K). Water temperature is approximately 250°C, and outside-tube temperature is around 325°C, both well below the safe limit of 525°C.

With a $CaSO_4$ scale of 0.15 mm thick, the temperature gradient across the scale is approximately 200 K in order to maintain the rate of formation of steam. This raises the external temperature of the steel from 325°C in the absence of any scale to about 525°C. This exceeds the safe temperature for steel in an air atmosphere, and at the steam pressure generated, it will result in tube failure.

Scale formation is thus a major problem of failure in steam boilers where hard water is used. Thermal conductivity of silicate scale is so low (0.0008 W/cm K) that a buildup of as little as 0.05 mm can cause boiler failure.

Scale formation can be prevented by removing salts which cause the scale or by adding substances which prevent the formation of scale in the boiler. A common additive is Na_3PO_4, though other phosphates such as NaH_2PO_4, Na_2HPO_4, and $Na_2P_2O_7$ are also used depending on the acidity of the water. Phosphate is added to the water at 25–50 mg/L to precipitate the calcium as the insoluble $Ca_3(PO_4)_2$. In small plants, additives such as tannin or starch are added to soften the scale, making it easier to remove after it has formed. EDTA can also prevent calcium and magnesium scale by complexing the cations. Similarly, EDTA can remove scale once formed.

A simple but as yet unexplained process of reducing scale formation is the use of a magnetic field of up to 7,000 G. The method was initially proposed in 1865, and several patents have been issued for what is also referred to as a magnetohydrodynamic effect. The most successful applications are those in which the magnetic field is at 90° (orthogonal) to the water flow. The crystal size and morphology of the $CaCO_3$ formed are influenced by the magnetic field. Various claims have been made by manufacturers of magnetic treatment devices, and these include not only the reduction in scale formation but also its removal.

Water treated with ozone tends to reduce scale formation because of the chelating compounds formed by the oxidation of the organic substances in the water. This aspect, though significant, is often of secondary consideration in choosing ozone for water treatment.

The cost of scale formation to US industry is estimated to be $10 Billion annually, and even a small reduction in boiler scale will result in large savings.

15.8 Wastewater

Industrial and municipal *wastewater* treatment is designed to permit the safe disposal of the discharged water. The important components of the contaminants are:

1. Suspended solids
2. Biodegradable organics
3. Pathogens
4. Nutrients
5. Industrial metals and organics

The cleanup is classified into primary and secondary treatment.

Primary treatment includes sedimentation and filtration which reduces the BOD by about 30%. The secondary treatment contains about 40% of the suspended solids and all of the dissolved metals and organic substances. Microorganisms can be used to remove the organics by aerobic digestion where pure oxygen is often used to accelerate the biological rate. The remaining dissolved organics and metals are removed by physical processes such as adsorption, by microporous membrane filtration, and by oxidation and precipitation. In some cases, further tertiary treatment is used to remove nitrogen and phosphorus compounds and other plant nutrients.

An interesting and novel approach to the treatment of wastewater has recently been developed by Delta Engineering (Ottawa) called the *Snowfluent* method. The process consists of three steps:

1. During freezing conditions, with outdoor temperatures below −6°C, the contaminated raw wastewater (from a storage lagoon) and compressed air are sprayed into the air forming fine droplets ($d < 200$ μm) which freeze and produce snow. The volatile components, CO_2, NH_3, H_2S, and some VOCs are released into the atmosphere, while the freezing of bacterial cells causes membrane ruptures, thus sterilizing the snow. When conducted during daylight, the UV contributes to an additional disinfection effect. At distances of 30 m from the spray, the odors are significantly reduced and considered not to be a nuisance.
2. The snowpack is aged during which time the BOD decreases further, and the pH increases while nutrients, such as phosphorus precipitate, do not redissolve when the snow melts. Organic particles also separate out forming a residue on melting.
3. The remaining process leaves runoff and residue as the snow melts. Meltwater can be released into neighboring freshwater systems or used for irrigation. In the case of animal waste treatment, the runoff can be stored in a holding pond for recycling as a flushing system for barns.

The few remaining surviving pathogens in the snowpack are destroyed by exposure to sunlight (UV) or are unable to reproduce due to ice damage. A diagram of the process is shown in Fig. 15.8. The cost of the Snowfluent process is from 10 to 25 cents/m^3 compared to \$0.50–\$1.50/m^3 for conventional wastewater treatment.

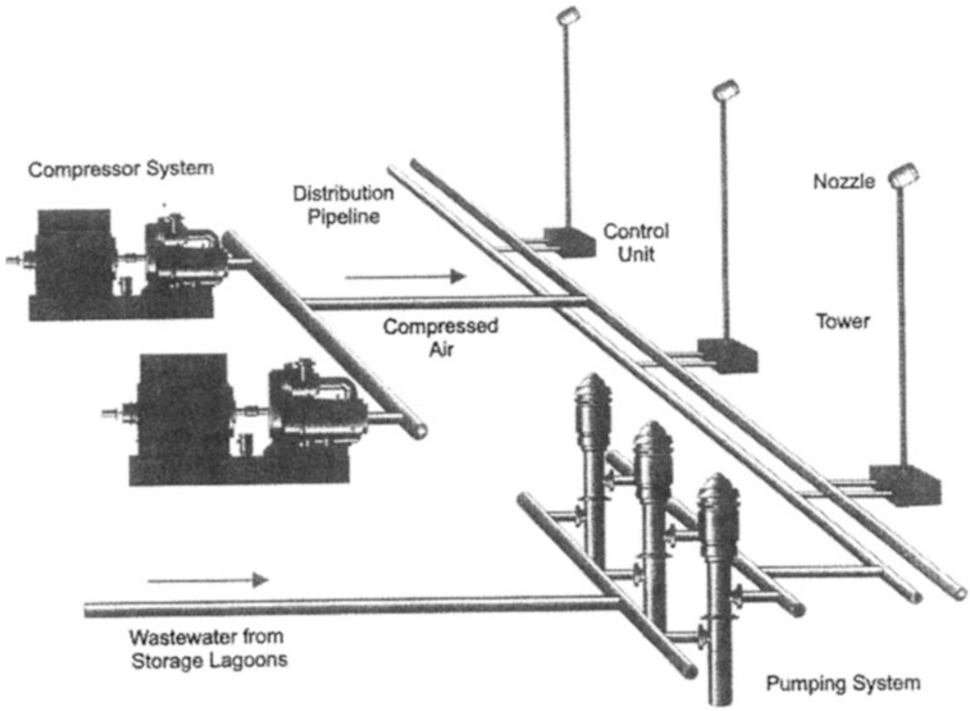


Fig. 15.8 Diagram of the basic components of the Snowfluent process which converts wastewater into sterile snow

A United Nations report has predicted that by 2025, two-thirds of the world's population will be facing water shortage. The need to conserve and recycle water cannot be overemphasized if mankind is to prosper in our limited global environment.

Exercises

1. What are the physical characteristics that determine water quality?
2. How are the quantities in Exercise 1 evaluated?
3. How is water made safe for drinking?
4. What six substances (in order of decreasing importance) would you want to have analyzed in your well water?
5. Write the hydrolysis reactions for alum and $FeCl_3$ used to clarify water.
6. What is hardness and how can it be determined?
7. How can the hardness of water be reduced?
8. Draw a diagram showing the EDTA complex for Al^{3+}.
9. Calculate the temperature gradient across a silicate scale of 0.1 mm thick if a heat flux of 40 W/cm^2 is required.
10. Speculate on the possible mechanism whereby a magnetic field influences the formation of scale.
11. Why is reverse osmosis so popular?
12. Calculate the amount of gold present in the oceans.
13. Explain how a nuclear-powered ship could successfully transport icebergs to desert lands.
14. What is the BOD and COD of a water sample?
15. Describe how gas hydrates (see Chap. 6) can be used in the desalination of seawater.

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