John A. Black

water pollution technology

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In this text I have attempted to bring together the total spectrum of information on marine, surface, and groundwater systems, the sources and consequences of pollution and possible solutions; as well as applications and the analytical methods commonly used in water and wastewater monitoring.

Since all aquatic systems operate by the same or similar chemical, physical, and biological principles, much of the information is interrelated and is as pertinent to deep oceans as it is to freshwater bogs. Hence many principles, methods, and applications are discussed extensively in earlier chapters and merely referred to in later sections. Also included are detailed sections explaining instrument use and standardization, as well as the pertinent analytical methods commonly used in pollution monitoring.

The reader will, therefore, obtain general background information as well as explicit analytical techniques and applications used in monitoring environmental pollutants, together with an understanding of the consequences of releasing these materials into waterways.

It is the author's opinion that this text may be used at a variety of instructional levels. For example, the general background information can be used in introductory environmental curricula; and, when combined with the applications and analytical techniques, the material is suitable for more advanced students.

I would like to express my appreciation to the many individuals and organizations for assistance during the preparation of this book. Special thanks to Fred Drewes, Ken Ettlinger, Jim Schramel, and Sue Stehlin of Suffolk County Community College, and to Ron Rozsa, a graduate student at the University of Connecticut for commenting on various portions of the preliminary manuscript and for helping with illustrations and photographs. I would also like to acknowledge the contributions of Violet Schirone of Suffolk County Community College for the material on microbiology, and Richard Horner of Northampton Area Community College for suggested additions to the sections deal-

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chemical and physical properties of water

Prior to discussing natural, aquatic, and marine systems, it is necessary to discuss the chemical and physical properties of the constituents that comprise these systems. Although the waters of the world contain many, if not all, of the chemical elements known to man, these elements have many commonly shared characteristics. Thus a consideration of the chemical and physical characteristics of these elements provides a convenient starting point for the study of water resources.

general physical—chemical principles

All matter is composed of electrically neutral atoms, and all atoms are composed of smaller components termed subatomic particles. Although physicists have discovered over 30 subatomic particles, only 3 need be **Considered here: the profon, the neutron, and the electron.

The proton is a positively charged particle located in the center of the atom in a region termed the nucleus. The proton is a relatively stable particle and has an assigned relative weight of 1. The neutron is also located in the nucleus, is neutrally charged but unstable, and also has an assigned relative weight of 1. Electrons are negatively charged, orbit the nucleus in a series of electron clouds, are relatively stable, and have an assigned relative weight of 1/1840th the weight of a proton or neutron. Since all atoms are electrically neutral, they must have the same number of electrons as protons in order to maintain electrical neutrality. The sum of the weights of these subatomic particles gives each atom its characteristic weight, which is termed the gram atomic weight of that atom. Since it is impossible to weigh and/ or work with individual atoms, chemists generally work with larger quantities, such as grams. To maintain a consistent relationship between atoms they use quantities termed moles. A mole of any substance is merely the gram atomic weight of that substance expressed in grams.

The number of protons contained in the nucleus of a particular atom, as well as the gram atomic weight of the atom, are conveniently determined from the *Periodic Chart* (Fig. 1-1). Note that each atom on the chart is represented by a symbol and that numbers appear both above and below the symbol for each atom. The number directly below the symbol represents the atomic weight of that element, while the number above the symbol gives the total number of protons contained within the nucleus. Since all atoms are electrically neutral, there must be an identical number of electrons circling about the nucleus in one or more electron clouds. For example, hydrogen is

listed on the periodic chart as H . The number 1 indicates that the

hydrogen atom has one proton in the nucleus and, hence, must have an electron cloud consisting of one electron. The lower number (1.008) is the gram atomic weight of the hydrogen atom. Thus if a chemist weighed out 1.008 grams (g) of hydrogen, 1 mole of hydrogen would be obtained.

Table 1-1 summarizes the characteristics of the subatomic particles. It is to be noted that the only basic difference among the various atoms is their size and weight, which is governed by the number of protons, electrons, and neutrons that comprise any given atom.

TABLE 1-1

	chara	ecteristics	of subatomic	particles		
Particle	Symbol	Charge	Relative Weight	Stability		
Proton	+	Positive	1	Stable		
Neutron	0	Neutral	1	Unstable		
Electron	e-	Negative	1/1840	Stable		

When two or more atoms react, they do so by completely or partially transferring electrons and thus forming molecules. In general, there are three basic types of chemical reactions that occur. The first type of reaction involves the complete loss of electrons by one atom or atoms and the complete gain of electrons by another atom or atoms within the molecule. In reactions of this type, the atom losing electrons (losing units of negative charge) becomes positive, because it has an excess of protons. The atom gaining electrons (gaining units of negative charge) becomes negative, since it has an excess of electrons. The molecules formed in these reactions are termed *ionic compounds*. A

ii N	2 He 4.0026	20. Ne 20. 18	18 Ar 39.95	36 Kr 83.80	54 Xe 131.30	86 74		
, =		9 F 18.998	17 Cl 35.46	35 Br 79.92	53 - 26.91	85 A1	71 Lu 174 98	
>		8 0 15.999	16 5 32.06	34. Se 78.96	52 Te 127.61	28 e	70 Yb	102 No
>		V N 14.09	15 P 30.98	33 As 74.91	51 Sb 121.76	83 8 209.00	69 Tm 168.94	101 Md
≥	· e	6 C 12.011	14 S. S.	32 Ge 72.59	50 Sn 118.70	82 Pb 207.21	68 Er 167.27	100 F.m
=		5 B 10.81	13 A! 26.98	31 Ga 69.72 7	49 In 114.82	81 Ti 204.39	67 Ho 164 94	99 E.s
			7	30 Zn 65.38 6	48 Cd 112.41	80 Hg 200.61 20	66 Dy 162.51	88.5
				29 Cu 63.54 6	47 Ag 107.88	79 Au 197.0 20	65 Tb	97 B.K
				28 Ni 58.71 6.	46 Pd 106.4 10	78 Pt 195.09	64 Gd 157.76	18 %
				27 Co 58.93 54	45 Rh 102,91 10	77 Ir 192.2 19	63 Eu 152.0	95 Am
						· · ·	62 Sm 150.35	26.0
	يِّ	<u></u>	7	26 Fe 55.85	44 Ru 101.1	76 Os 190.2	P _m	N 93
	Atomic number	Element Atomic mass		25 Mn 54.94	43 Tc	75 Re 186.22		
]	24 Cr 52.01	42 Mo 95.95	74 W 183.86	60 Nd 144.27	
	Legend			23 V 50.95	41 Nb 92.91	73 Ta 180.95	59 Pr.	+
				22 Ti 47.90	4u Zr 91.22	72 Hf 178.50	58 Ce 140.13	90 Th 232.04
			.,	21 So 44.96	39 Y 88.92	57 La* 138.92	89 Ac*•	£
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principal quantum number j		~	n	4	2	· · · · ·		
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typical ionic compound is formed as the result of the reaction between sodium (Na) and chlorine (Cl) in which the sodium chloride molecule (NaCl) is formed. In this reaction electrons are lost by the sodium and gained by the chlorine. This transfer of electrons gives sodium a positive charge and chlorine a negative charge. The resultant molecule may be represented as $Na^+ \rightarrow Cl^-$, with the arrow serving to indicate the direction of electron movement.

The second type of reaction involves the complete and equal sharing of electrons. Reactions of this type occur only between identical atoms. In these reactions the electrons are equally shared, so no charge develops on any of the atoms comprising the molecule. These molecules are termed nonpolar, covalent molecules. A typical molecule of this type is hydrogen gas (H_2) , in which two hydrogen atoms come together and equally share electrons. Since the electrons are shared by identical atoms, there is no tendency for one atom to attract electrons more or less strongly than the other, and no charge develops. This molecule may be pictured as $H \longleftrightarrow H$.

The third type of reaction involves the unequal sharing of electrons between the atoms that comprise the molecule. The atom or atoms that partially lose their electrons assume a partial positive charge, whereas the atoms that partially gain the electrons assume a partial negative charge. Molecules formed in this manner are termed polar, covalent molecules. A typical polar covalent molecule is water (H_2O) , in which the two hydrogen atoms partially lose their electrons to an oxygen atom. Thus the hydrogen atoms assume a partial (α) positive charge, and the oxygen assumes a partial negative charge. The molecule may be represented as $H^{a+} \rightarrow O^{a-} \leftarrow H^{a+}$.

chemical and physical properties of water

In the case of the water molecule it has been found that, in addition to its being polar, the atoms are arranged in a bent-chain configuration. The water molecule will, henceforth, be pictured as +/->+, where the positive regions (actually partially positive) are the hydrogen atoms, and the negative regions (actually partially negative) are the oxygen atoms.

Because of its polarity, water molecules tend to arrange themselves in a definite, ordered manner. This is due to the fact that the positive region of one molecule attracts the negative region of an adjacent molecule, forming a relatively weak intermolecular attractive force termed a hydrogen bond. The positive ends of this molecule will then form hydrogen bonds with the negative region of still another molecule, and so on. The end result can be visualized as a long series of water molecules arranged so that the positive ends of various water molecules are aligned with the negative ends of adjacent molecules, and vice versa. This is schematically illustrated in Fig. 1-2A.

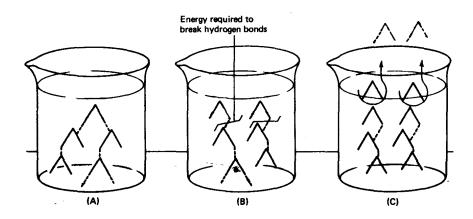


FIGURE 1-2

(A) Schematic representation of a group of hydrogen-bonded water molecules. (B) Sufficient energy must initially be added to break the hydrogen bonds. (C) Additional energy must then be added to allow the molecules to break through the surface and enter the vapor state.

hydrogen bonding

Hydrogen bonds are of the utmost importance in giving water its unique chemical and physical properties. This is readily illustrated by considering the phenomenon that occurs when a given liquid is brought to its boiling point. In order to boil a liquid, energy must be added. The energy, in the form of heat, is absorbed by the liquid and serves to increase the molecular motion of the molecules comprising the liquid. Once the molecules are moving at a sufficient rate, they are able to break through the surface of the liquid and enter the vapor state. At this point the liquid is said to boil. In the case of a polar liquid, such as water, sufficient energy must not only be added to achieve the stage of high molecular motion, but, prior to reaching this stage, initial energy must be put into the system to first break the hydrogen bonds that hinder free molecular motion of the molecules within the liquid (Fig. 1-2B and C). For example, if it requires four

units of energy to place the molecules in the vapor state, an additional initial amount of energy must be added to break the hydrogen bonds. Consequently, that liquid would have a high boiling point (a higher temperature would be required to make the liquid boil). It has been calculated that if water were a nonpolar liquid, it would have a boiling point of approximately $-80^{\circ}\mathrm{C}$ rather than its normal boiling point of $100^{\circ}\mathrm{C}$. In other words, if water were nonpolar, it would be a vapor at normal earth temperatures.

density

The relationship of hydrogen bonding to temperature is extremely important in natural systems and can be related by the concept of density. Density is the relationship of the mass (M) of any given material to the volume (V) occupied by that material. This can be expressed by the formula D = M/V. According to this equation, density can be changed by altering the weight (mass) or volume of a substance. For example, if a liquid has a mass of 10 g and occupies a volume of 10 liters, its density would be 1 (D = M/V) or D = 10/10= 1). If, on the other hand, the volume remains constant at 10 liters and the mass is decreased to 5 g, the density would decrease to 0.5 (D = 5/10 = 0.5). Thus the density of a particular substance will increase if the mass is increased and the volume kept constant, or if the volume is decreased while the mass remains constant (or increases). Conversely, the density will decrease if the mass is decreased and the volume held constant (or increased), of if the volume is increased and the mass is held constant (or decreased). Table 1-2 summarizes the possibilities.

TABLE 1-2

means of changing density

Assuming that the initial conditions are as follows: M = 2 g; V = 10 liters; D = 2/10 = 0.2

Factors increasing D:

1. If M is increased to 4 g with V remaining constant (10 liters)

2. If M is constant (2 g) with V decreased to 5 liters

Factors decreasing D:

1. If M is constant (2 g) with V increased decreased to 20 liters

2. If M is decreased to 1 g with V constant (10 liters)

D = 4/10 = 0.4; density is increased to 0.4

D = 2/5 = 0.4; density is increased to 0.4

D = 2/20 = 0.1; density is decreased to 0.1

D = 1/10 = 0.1; density is decreased to 0.1

temperature

As noted previously, hydrogen bonding plays an important role in determining the density of natural marine and freshwater systems. This role is established through the effects of temperature on the formation and amount of hydrogen bonds formed within a given system. The degree of hydrogen bonding will affect the volume of a given system, and this, in turn, will affect the density. As discussed previously, energy, in the form of heat, must be added to water to not only allow the molecules to attain sufficient speed to enter the vapor state, but (initially) sufficient heat must also be added to break the hydrogen bonds which prevent unrestricted movement of the individual water molecules. Thus by raising the temperature of the liquid water, hydrogen bonds are broken and the molecules can move about more freely. In other words, molecular motion is increased. By increasing molecular motion, the distance between the individual molecules is increased. This increases the volume occupied by the liquid and decreases the density. In general, the higher the temperature of any given system, the lower the density. The reverse occurs when a liquid is cooled. As the temperature is decreased, the molecules move more slowly. Since molecular motion is decreased, hydrogen bonds can be easily formed between adjacent, slow-moving molecules. Since increased hydrogen bonding restricts the molecular motion even further, less volume is occupied by the liquid. As the volume decreases, the density must increase.

The effects of temperature on hydrogen bonding, and thus on density, can be illustrated by considering the phenomenon that occurs when water is cooled from a very high temperature to 0°C. Assume a hypothetical case where 10 g of water is present in a sealed 1-liter container at a temperature of 105°C (this is above the boiling point and, therefore, all the water can be considered to be in its vapor state). With all the water in the vapor state, the water is considered to be effectively occupying the entire container, since the pressure exerted by the water is identical on all the walls of the container. This pressure is exerted by the water molecules, moving independently and colliding with the walls of the container. At such a high temperature it can be assumed that there are no hydrogen bonds present in the system. If the container is cooled to 90°C, for example, the water molecules would begin to slow down. As their speed decreases should one water molecule, at this lower temperature, encounter another molecule, there is a good probability that they would tend to form hydrogen bonds and become "heavier" than the medium in which they are floating. At this point the water will condense (go into the liquid state). For purposes of illustration, assume that at 90°C essentially all the molecules have formed hydrogen bonds to some degree, all the water is in the liquid state, and the molecules, at this temperature, now occupy only 75% of the container (the volume has decreased to 0.75 liter). Since the container is sealed, no molecules escape or enter; and the mass has therefore remained constant while the volume has decreased, owing to the condensation of the water vapor, and the density has increased (Fig. 1-3).

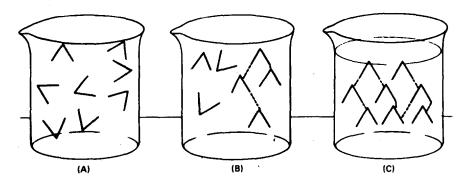


FIGURE 1-3

(A) Schematic representation of water at 105°C. Note that all of the molecules are moving independently and that hydrogen bonds are absent. At this point the water is effectively occupying the entire container. (B) As the water is cooled below the boiling point, hydrogen bond formation begins. The water will begin to condense and enter the liquid state. (C) At this point condensation is essentially complete. The water is in the liquid state, and the volume occupied by the water has decreased.

If the temperature is lowered to 50°C there will be even less energy to move the molecules about. Consequently, more molecules will be moving at a lower speed (in the liquid state) and more hydrogen bonds will be able to form. Since hydrogen bonding is increased further, molecular motion is decreased, and this will result in a decreased volume. As the volume decreases, the density will increase further, and the liquid will become "heavier." In reality, however, the mass is not increasing; rather, the same number of molecules are, at this stage, packed into smaller and smaller space. Thus the volume is decreasing and the density is increasing.