5 Water Composition

Water itself, as we shall see, is easily the most extraordinary and complex substance known to man, anomalous in all of its physical-chemical properties.

R.A. Horne, *Marine Chemistry*

5.1 INTRODUCTION

Sea water is a complex solution of dissolved minerals, elements, and salts. Virtually all of the known stable elements are found in sea water, although sometimes in only very minute concentrations. Because water is a compound of hydrogen and oxygen (H_2O), these two are the most abundant elements. Sodium chloride (common salt, $NaCl$) makes up the vast majority of all the dissolved salts. Sodium bicarbonate and sodium sulfate along with magnesium, calcium, and potassium chlorides and sulfates make up most of the rest. In most of the oceans, the ratio between these various ions is remarkably constant (a result known as *Dittmar's law*), but it is sometimes forgotten that this may not be true in some coastal areas. River waters have saline composition different from ocean water so that coastal areas near major river mouths may have a different ratio of ions.

The hydrostatic variables of importance are density (ρ) and pressure (p) of water, two variables that are related through the hydrostatic equation:

$$p = \rho g z \tag{5.1}$$

where g is the acceleration due to gravity (9.8 m s^{-2}) and z is the depth. Typical seawater densities are around 1.025×10^3 kg m^{-3} so that a depth increase of 1 m is very close to a pressure increase of 10^4 Pa, where the Pascal, or Newton per square metre, is the official SI unit of pressure. In everyday conversation the oceanographer uses the decibar (1 bar = 10^5 Pa) almost synonymously with the metre, and, as there is no convenient SI term to cover 10^4 Pa, the oceanographic community has strongly resisted the complete introduction of SI metrication. Of course, many old sailors still yearn for the fathom (1 fathom = 6 ft = 1.829 m) because it was the length of their outstretched arms when laying out a lead line to measure depth.

Density is influenced principally by the temperature and dissolved salt content of water. Since it is relatively easy to measure accurately water temperature and salinity but rather difficult to measure density with the precision required in oceanographic work, salinity and temperature are the two prime physical quantities that must always be determined in any oceanic or estuarine investigation. They provide useful information in their own right, as we shall see, but if they are taken together

to compute the water density then dynamicists can calculate the stability and flow characteristics of the water. These can then be checked by direct measurements of water movement.

5.2 DENSITY

5.2.1 PURE WATER

Pure water at 4°C has a density very close to 1.0 gram per cubic centimetre ($g\ cm^{-3}$), or 1000 kilograms per cubic metre ($kg\ m^{-3}$). It is actually 999.97 $kg\ m^{-3}$. This is the maximum density which *pure* water can have. If it is heated, its density will decrease — hot water convects to the surface in a heated saucepan. If it is cooled below 4°C, its density will decrease — ice floats.

Oceanographers are primarily interested in small variations in density and have established a convention whereby:

$$\sigma = \rho - 1000 \qquad (5.2)$$

where ρ is the numerical value of the density in $kg\ m^{-3}$. Thus, for a density $\rho = 1025.03\ kg\ m^{-3}$, $\sigma = 25.03$.

The quantity σ (sigma) is called the *density excess* or the *Knudsen parameter*. Its exact definition, symbol, and nomenclature continue to be under debate in the oceanographic community, so that in highly accurate density calibrations one needs to explicitly state the definition used. For most work, Equation 5.2 is adequate, and in coastal oceanography σ is identical to a quantity σ_t (sigma-tee) that often crops up in deep sea oceanography.

The specific volume is the reciprocal of the density, $1/\rho$, and in many theoretical calculations it is of greater convenience. Just as the variations in oceanic density are small, the variations in specific volume are small. For example, when $\sigma = 25.03$, the specific volume is 0.97558 cm^3/g or $9.7558 \times 10^{-4}\ m^3/kg$.

5.2.2 SALINE WATER

The addition of salt increases the density of water if the temperature remains constant. The oceanographic literature has many formulae for calculating the density excess or the steric anomaly (i.e., the departure of the specific volume from a conveniently chosen reference value). There is no single, simple formula that gives either of these parameters exactly for all values of salinity, temperature, and depth. There is, however, an internationally agreed standard known as the International Equation of State for Seawater. The *Applied Environmetrics Oceanographic Tables* provides a computer disk that will produce tables based on it.

Mathematical formulae for the density excess or the specific volume are usually based on quadratic or higher order curves fitted about the particular salinity and temperature of interest. Formulae for oceanic work are liable to be inaccurate if applied to the density of water in rivers or estuaries. Indeed, for many situations
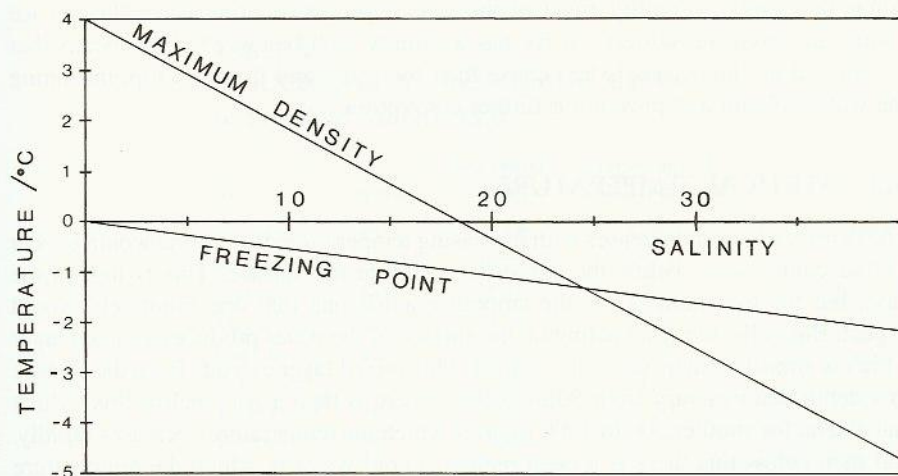
FIGURE 5.1   Salinity dependence of the freezing point of water and the temperature of maximum density: the intersection of the curves, at a practical salinity of 25, represents a change in the freezing properties of saline water. (Based on data in UNESCO, *National Oceanographic Tables,* National Institute of Oceanography, Great Britain, and UNESCO, Paris, 1966. Updated by W. Wilson and D. Bradley, *Deep Sea Res.,* 15, 355–363, 1968; R.G. Perkins and E.R. Walker, *J. Geophys. Res.,* 77, 6618–6621, 1972.)

one's interest lies in small density variations about a particular density, and a straight line fit is an adequate approximation.

The addition of salt to water markedly affects the water properties. The maximum density of a salt solution occurs below 4°C. The presence of salt lowers the freezing point. This is why Canadians sprinkle salt on their winter roads. Figure 5.1 shows the relation between the freezing point and the temperature of maximum density for water as the salinity increases. There is a crossover point at −1.33°C and a practical salinity of 24.695, which has important consequences in the freezing patterns of low and high saline waters.

5.2.2.1   Low Salinity Waters (Lakes, the Baltic Sea)

At low temperatures, these waters circulate with the colder water, near 4°C, dropping to the bottom until the entire water body is at the temperature of maximum density. Further cooling then lightens the topmost water, which does not sink. The topmost water then cools rapidly and ice forms at the top surface.

5.2.2.2   High Salinity Waters ($S > 25$)

In this case, convection should continue until the entire water column is at the freezing temperature, and the whole water column then freezes. Because of the vast heat extraction required to cool a 4-km depth of ocean water to its freezing temperature, this type of freezing could only occur in the shallower parts of the Arctic and

Antarctic waters. In reality, most of the salt drops out as brine when the sea ice forms, and even the saltiest sea ice has a salinity well below 25. This means that ice formed on the oceans is less dense than the water and floats on top, insulating the water column and preventing further convection.

5.3   VERTICAL TEMPERATURE

The density of water decreases with increasing temperature; hence, one would expect to find colder water below the sea surface than at the surface. This is indeed the case, but the transition is not the smooth gradual one that one intuitively would expect. Basically, the wind acting on the surface of the water produces a mixed layer which is almost isothermal in the vertical. This mixed layer extends from the surface to a depth that can vary from 50 to 200 m. There is then a zone below this, which can extend for another 500 to 1000 m, over which the temperature decreases rapidly, and then below this there is a deep region of cold water in which the temperature decreases very slowly.

The depth interval in which the relatively rapid transition between the warm waters of the upper mixed layer and the cold bottom water occurs is called the *thermocline*. Detailed studies of the upper waters reveal that, in fact, the temperature distribution consists of a large number of mini-thermoclines. In low and middle latitudes there is a distinct thermocline present at all times at depths between 200 and 2000 m. This is referred to as the "main" or "permanent" thermocline. It is rarely found in coastal waters, and then only during upwellings when constant temperature surfaces — isotherms — tilt upwards as cold water rises from the depths (more about upwellings in Chapter 7).

5.4   SALINITY

Salinity of water is an important term in the equation of state (i.e., the formula linking density, temperature, and salinity). If the sea were composed of only one type of salt (e.g., NaCl), then there would be little problem in defining salinity in terms of the weight of dissolved salt per unit weight of sea water. In fact, sea water is a mixture with a most remarkable property: the ionic ratios in sea water are virtually the same, with the composition shown in Table 5.1, wherever and whenever readings are taken, provided only that they are not taken close to the discharge of a large river. The remarkable constancy in the ionic composition of sea water is evidence of a continual, and highly effective, mixing taking place on geological time scales in the world's oceans. There are a number of different recipes for producing synthetic sea water which can be used without the complicating effects of suspended, organic, and biological material that are present in real sea water. The most recent combines 23.926 g NaCl, 4.008 g Na_2SO_4, 0.677 g KCl, 0.196 g $NaHCO_3$, 0.098 g KBr, 0.026 g H_3BO_3, 0.003 g of NaF plus 53.27 ml of a 1.0 M $MgCl_2$ solution, 10.33 ml of a 1.0 M $CaCl_2$ solution, and 0.90 ml of a 0.1 M SrO_2 solution with sufficient pure water added to make a total weight of 1 kg.

TABLE 5.1
**Ionic Composition (by weight) in Sea Water
of Practical Salinity 35.0**

Ion	Symbol	Sea Water (g/kg)	Percentage of Dissolved Salts
Chloride	Cl^-	19.35	55.04
Sodium	Na^+	10.77	30.62
Sulfate	SO_4^-	2.71	7.71
Magnesium	Mg^{++}	1.29	3.68
Calcium	Ca^{++}	0.41	1.17
Potassium	K^+	0.40	1.14
Bicarbonate	HCO_3^-	0.12	0.33
Bromine	Br^-	0.07	0.19

*Source:* Based on F.J. Millero, *Ann. Rev. Earth Planetary Sci.*, 2, 101, 1974.

On the basis of the chloride ion concentration, the definition of salinity was originally based on its determination by chemical titration with silver nitrate so that salinity was defined historically as 1.80655 times chlorinity. In late 1979, this definition was officially abandoned and a new definition for salinity was introduced based on electrical conductivity. This is now termed the *practical salinity* in order to distinguish it from the absolute salinity, which is the ratio of mass of dissolved material in a seawater sample to the mass of the sample.

Practical salinity is plotted on a practical salinity scale, an example of which is given in Figure 5.2. The scale is based on a standard sea water having, at 15°C and under normal atmospheric pressure, an electrical conductivity equal to that of a standard potassium chloride solution containing 32.4356 g of KCl per kg of solution. This particular standard sea water comes from the North Atlantic and used to be known as *Copenhagen water*. Its chlorinity equals 19.374×10^{-3}, and it has received a practical salinity value equal by definition to exactly 35. Note that the practical salinity is **not** 35×10^{-3}, or 35‰; practical salinity has been defined so as to have a numerical value 1000 times larger than the absolute salinity.

In electrical conductivity units, pure water with a salinity of zero has zero conductivity. At a practical salinity of 35 its conductivity is 4.29 Siemens per metre (S/m) at 15°C or 2.904 S/m at 0°C.

5.4.1 SALINITY DISTRIBUTION

The salinity distribution at the surface of the world's oceans is almost completely controlled by the world's rainfall pattern. Regions of high rainfall and low evaporation near the Equator have low surface salinity due to rainfall dilution of the waters. Regions of low rainfall, namely those situated in the vicinity of the subtropical high pressure zone between 20° and 40° latitude, have high surface salinity due to marked
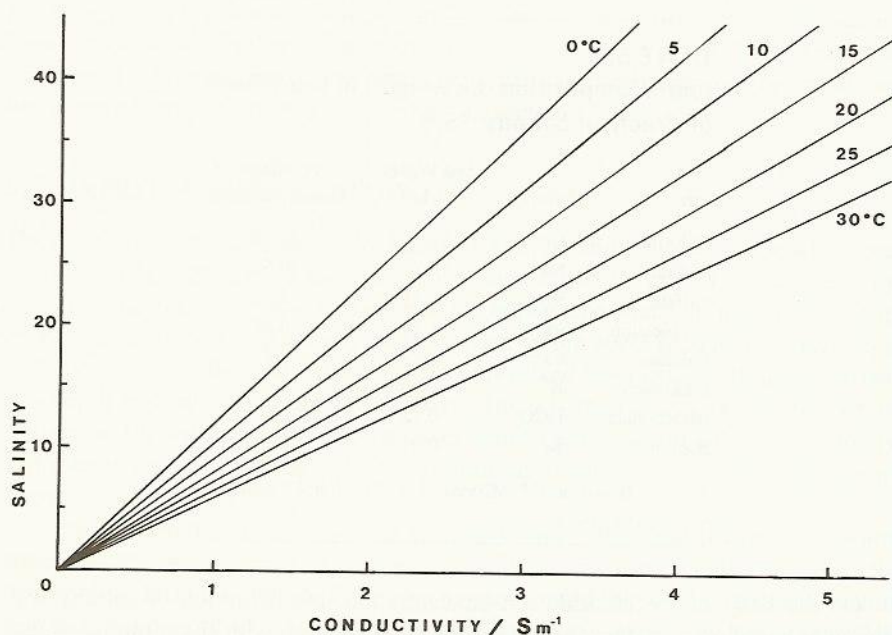
FIGURE 5.2 Practical salinity scale relating salinity to conductivity as a function of temperature. (Based on data in UNESCO, *National Oceanographic Tables,* National Institute of Oceanography, Great Britain, and UNESCO, Paris, 1966. Updated by W. Wilson and D. Bradley, *Deep Sea Res.,* 15, 355–363, 1968; R.G. Perkins and E.R. Walker, *J. Geophys. Res.,* 77, 6618–6621, 1972.)

evaporation of the surface waters. The salinity distribution in the vertical direction is variable. It is the density that controls the vertical distribution of water, with the less dense water overlying more dense water.

As a rough and ready rule of thumb, a salinity increase of 1 produces much the same density change as a 4°C decrease in temperature. In offshore waters, the salinity range is normally small, and it is predominantly temperature that controls the density. In estuaries there can be a relatively sharp transition between salt and fresh water. This is known as a *halocline*, in the same way that a sharp change in temperature is a thermocline. Generally, haloclines and thermoclines are identified with pycnoclines as well — a region in which the density changes sharply.

A pycnocline then will be a thermocline, a halocline, or both, and it is only worth using the term in this latter situation. Conversely, in special circumstances one may have a region in which there is both a thermocline and a halocline but no pycnocline. This can occur when two bodies of water with identical densities but different temperature and salt compositions come together. Because heat and salt mix at different rates, the boundary will undergo a complicated mixing process, which will be examined in more detail in Chapter 8.

5.4.2 Temperature-Salinity Diagrams

Water that originates in a particular region possesses a distinctive salinity and temperature and tends to retain them as it moves. Polar waters have low temperature and salinity; mid-latitude waters have high salinities. Salt and heat diffuse very slowly so that these properties can be used as tracers of subsurface waters.

Water mass identification is usually done by plotting a diagram of temperature and salinity known as a *TS diagram*. This gives the temperature and salinity of the entire water mass from top to bottom. In Figure 5.3, there are at least three water types present. Warm, low-salinity water (tropical surface water) at about 28°C, S = 35; cooler, high-salinity water (Atlantic central water) at about 18°C, S = 35.6; and cold, low-saline water (subarctic water) near the bottom, 6°C, S = 34.7. If there was no diffusion and no mixing between these three water types, the TS diagram would consist of three isolated dots. In fact, mixing and diffusion spread the results into the typical curve of Figure 5.3.

In addition, the TS diagram has at least two further uses. First, a TS diagram provides a graphical method for determining density at a particular temperature and salinity. As shown in Figure 5.3, the shape of the isopycnals (lines of constant density) is a curved line, convex towards the T axis. Second, the TS diagram is extremely useful for data verification, and any data point that lies well off the historically determined TS curve is almost certain to be erroneous. Suspect data points have been boxed in Figure 5.3.
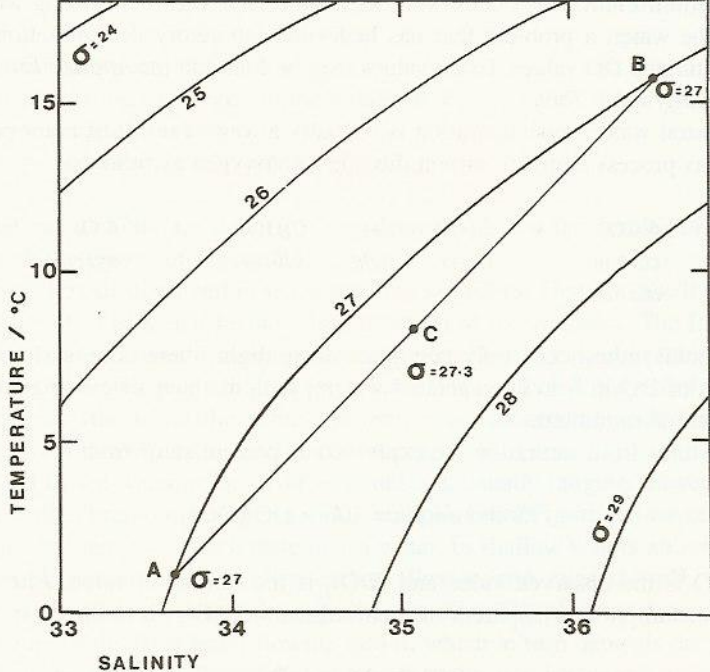
5.4.3 Cabbeling

The lines of equal σ on a TS diagram are slightly curved downward, as well as being inclined to the coordinate axes (Figure 5.4). Thus, when two water types of different salinity and temperature lie side by side and have precisely the same density — as indicated by points A and B on Figure 5.4 — their mixture will be represented by a point on the straight line joining their positions on the TS diagram. If they mix in equal proportions the mixture would be represented by the point C.

Because all points on the line joining A and B lie on the concave side of the isopycnal line of constant σ, the mixture must be slightly more dense and thus heavier than either of the two parent water types. It tends to slowly sink. Sinking due to this mixing process is known as *cabbeling* or *caballing*; we may note that in those areas where it occurs, it will help to maintain a discontinuity between the two different water types and hence maintain a sharp front between them.
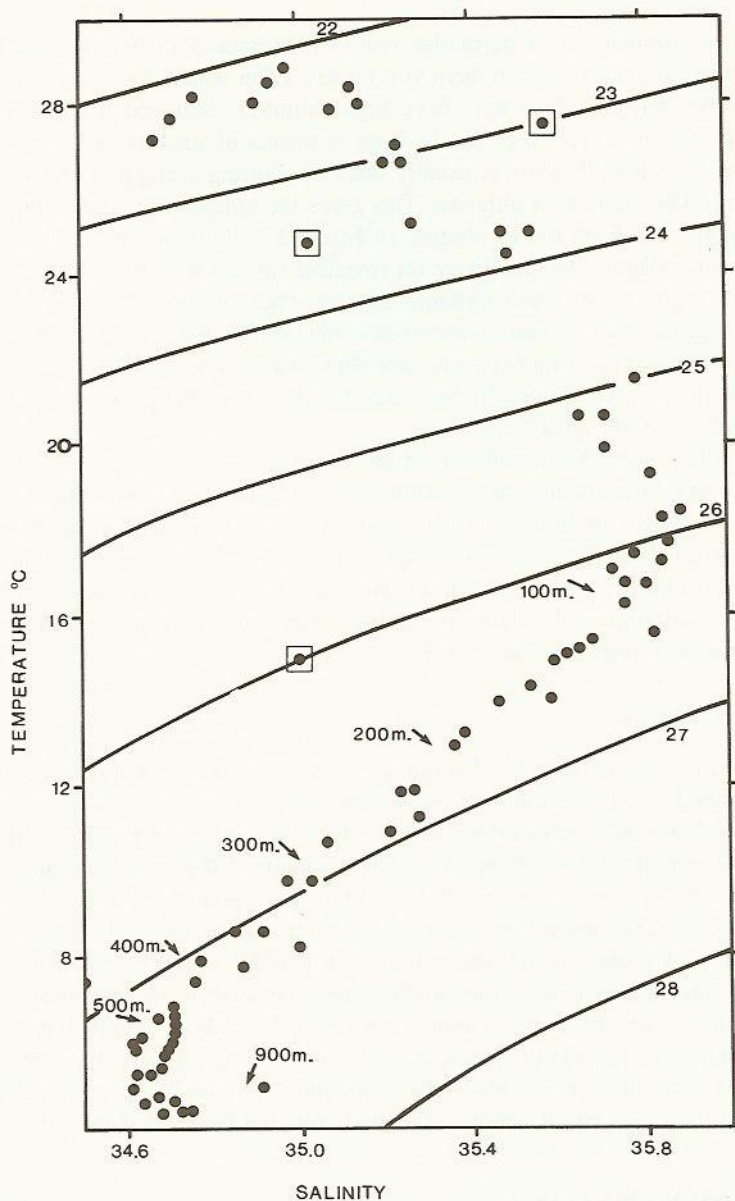
FIGURE 5.3 TS diagram for waters near the coast of Ghana, West Africa. Suspect data points are boxed. The solid lines are isopycnals joining constant values of density. The value of σ is indicated on the line. (Based on R.W. Houghton, *J. Phys. Oceanogr.*, 6, 909–924, 1976.)

FIGURE 5.4 Cabbeling consists of mixing waters of equal density (A and B) to produce a mixture of greater density (C) which then sinks.