CHAPTER VI

Chemistry of Sea Water

If suspended solid material of either organic or inorganic origin is excluded, sea water may be considered as an aqueous solution containing a variety of dissolved solids and gases. Determination of the chemical nature and concentrations of the dissolved substances is difficult for the following reasons: (1) some of the dissolved substances, such as chloride and sodium ions, are present in very high concentrations, while others, certain metals for instance, are present in such minute quantities that they have not been detected in sea water, although they have been found in marine organisms or salt deposits; (2) two of the major constituents, sodium and potassium, are extremely difficult to determine accurately; (3) it is virtually impossible in some cases to separate related substances such as phosphate and arsenate, calcium and strontium, and chloride, bromide, and iodide. In these cases the combined elements are determined together and usually reported as if they represented only one; that is, calcium and strontium are often calculated as "calcium," and chloride, bromide, and iodide as "chloride."

Because of the complex nature of the dissolved materials in sea water a specially developed technique is usually required to determine the concentration of any constituent. The standard methods for the quantitative analysis of solutions which are given in textbooks generally cannot be applied to sea water without adequate checks on their accuracy. This is particularly true when dealing with elements present in extremely low concentrations, because the elements occurring as impurities in the reagents may be in amounts many times those found in the water.

Constancy of Composition

It has been found that, regardless of the *absolute* concentration of the total solids, the *ratios* between the more abundant substances are virtually constant. The importance of this result cannot be overemphasized, as upon it depends the validity of the chlorinity:salinity:density relationships and, hence, the accuracy of all conclusions based on the distribution of density where the latter is determined by chemical or indirect physical methods such as electrical conductivity or refractive index.

The relative uniformity in the composition of the sea water was established by the investigations of Forchhammer, Natterer, and Dittmar. Although Forchhammer analyzed a large number of samples, his investigations were not complete because he did not determine certain of the abundant elements. Natterer made more detailed analyses, but it was Dittmar who laid the solid foundation for the present knowledge of the composition of sea water.

Dittmar (1884) made careful determinations on 77 water samples, representative of all oceans, which had been collected on the voyage around the world of H.M.S. *Challenger*. He determined the halides, sulphate, magnesium, calcium, and potassium. On composite samples he found the ratio of bromine to chlorine and estimated the carbonate. From the sums of the chemical equivalents of the negative and positive ions, he calculated the sodium by difference. This procedure was followed because he was unable to achieve satisfactory direct determinations for sodium. The results of Dittmar's work showed that there were no significant regional differences in the relative composition of sea water; consequently his average values could be used to represent the ratios between the major dissolved constituents. In table 33 are given Dittmar's average values in the units in use at the present time and referred to a chlorinity of 19.00 $^{0}/_{00}$. The percentages of the various ions are also shown.

TABLE 33

DITTMAR'S VALUES FOR THE MAJOR CONSTITUENTS OF SEA WATER

(Values in grams per kilogram, $^{0}/_{00}$)

Ion	Original values		Recalculated, 1940 atomic weights		1940 values	
	Cl = 19 $^{0}/_{00}$	%	Cl = 19 $^{0}/_{00}$	%	Cl = 19 $^{0}/_{00}$	%
Cl^-	18.971	55.29	18.971	55.26	18.980	55.04
Br^-	0.065	0.19	0.065	0.19	0.065	0.19
$SO_4^{=}$	2.639	7.69	2.635	7.68	2.649	7.68
$CO_3^{=}$	0.071	0.21	0.071	0.21	......	.....
HCO_3^-	......	.....	......	.....	0.140	0.41
F^-	......	.....	......	.....	0.001	0.00
H_3BO_3	......	.....	......	.....	0.026	0.07
Mg^{++}	1.278	3.72	1.292	3.76	1.272	3.69
Ca^{++}	0.411	1.20	0.411	1.20	0.400	1.16
Sr^{++}					0.013	0.04
K^+	0.379	1.10	0.385	1.12	0.380	1.10
Na^+	10.497	30.59	10.498	30.58	10.556	30.61
Total	34.311		34.328		34.482	

Since 1884 the modification of atomic weights has affected the numerical results reported by Dittmar. Corrections for these changes may be made (Lyman and Fleming, 1940) as shown in the "recalculated" values in table 33. In the latter tabulation the sodium has been recalculated by difference.

It is interesting to compare Dittmar's results with those obtained by modern methods of analysis as shown in the last columns of the table. The sources of these data are indicated in table 35. It is immediately seen that there are small differences for most of the elements determined by Dittmar and that certain other ions have been added to the list of major constituents. The bound carbon dioxide is reported as bicarbonate ion instead of as carbonate, strontium is given by itself instead of in combination with calcium, and fluoride and boric acid have been added.

The close agreement between the results of Dittmar and those obtained recently is remarkable when we consider the complexity of the problem and the great advance in knowledge of analytical chemistry. However, although the differences are small, they are significant, and hence the importance of Dittmar's work is that it showed the constancy of the ratios between the major constituents, and not that it led to accurate numerical values of these ratios.

In table 33 the composition is shown by referring the substances to a standard concentration, Cl = 19.00 $^0/_{00}$, and by means of the ratios between the different ions and the total dissolved solids. In most instances it is preferable to use a third method; namely, to give the ratios between the various substances and the chlorinity or the chlorosity (p. 52), and these ratios are known as Cl-ratios and chlorosity factors, respectively. The Cl-ratio is the amount of any ion or substance per unit (gram) of chlorinity, and is obtained by dividing the concentration in grams per kilogram by the chlorinity, or the concentration in grams per 20°-liter by the chlorosity. Multiplication of the Cl-ratio by a given chlorinity or corresponding chlorosity will give the concentrations as grams per kilogram or per liter, respectively. Concentrations in milligram-atom units are always on a liter basis, and, if divided by the chlorosity, yield the ratios that are called chlorosity factors. It may be noted that a chlorosity factor multiplied by chlorinity yields the concentration in milligram-atoms per kilogram.

The uniformity of relative composition in the oceans is the result of circulation and mixing. These operations are continuous, and tend to eliminate regional differences in composition, whatever the cause. Disturbing agencies bring about changes that are small compared to the bulk of the substances present and consequently will not materially affect the relative concentration of the major constituents. Furthermore, many of the disturbing processes that tend to modify the relative composition are reversible. For example, the secretion of calcium carbonate by organisms, which reduces the quantity of calcium in solution, takes place at a certain season or in certain parts of the sea, but upon the death of the organisms the calcium carbonate may dissolve in other regions. Although small regional differences may result from such processes, the effects are largely neutralized by mixing. On the basis of parallel determinations of density by means of interferometer (p. 54) and chlorine titration, Lotte Möller (Bein, Hirsekorn, and Möller, 1935) has shown that very small systematic differences exist in the composition of water masses of the North Atlantic, but as yet these are significant only as refined means for tracing water masses of certain characteristics.

The constancy of composition is, as already emphasized, of the greatest importance. Not only is it the basis of the chlorinity:salinity: density relationships, but it also affords a means of estimating the concentrations of all of the major constituents when the concentration of any one of them is known. Furthermore, results of studies on the composition or the physical properties of sea water in any locality are generally applicable to the water in any other part of the oceans.

Except in special areas, such as in the Baltic Sea, the Black Sea, and off the mouths of large rivers, it is not necessary to consider that the water represents special local types with properties that differ from those of sea water in general. Nevertheless, it should be remembered that the composition is not absolutely constant even for the major constituents listed in table 33. Various factors which will be discussed in detail later are always operating and always tend to modify the relative abundances. Rivers introduce dissolved material in proportions that are markedly different from those in the sea, and they also introduce sedimentary material that reacts in various ways with the dissolved constituents. The formation and melting of sea ice may bring about a modified distribution of the dissolved substances.

Thus far, comment has been largely restricted to those constituents of sea water that are present in large, or at least relatively constant, proportions. If we consider those elements which are present in small quantities and which are utilized by marine organisms, the concept of constant composition is no longer generally valid, because the concentrations of these elements vary widely, particularly near the surface. A great part of the work in chemical oceanography is now devoted to determining the space and time variations in variable constituents, and much thought is directed toward the solution of the problems related to the processes that control the observed distribution.

Units Used in Chemical Oceanography

In chemical oceanography most of the numerical results are expressed as concentrations—that is, as the amounts of various constituents in a certain quantity of sea water. Obviously many different combinations of mass and volume units are possible and, in fact, a great variety have been used. In order to avoid confusion and to make the results of different workers directly comparable, it is desirable that a standardized system of units for reporting results in chemical oceanography be followed. Such a system has been proposed by the International Association of Physical Oceanography (1939).

Only two units are to be used for expressing the quantity of sea water: either (1) the kilogram or (2) the amount of water which at 20° C. and pressure one atmosphere occupies the volume of one liter. The latter unit is designated as L_{20}, but in this discussion it will be indicated as L. The system in which the constituents are reported as the amounts present per liter is designated as the "preferred" one, with an alternative for the abundant substances that may be reported as grams per kilogram of sea water. Salinity and chlorinity are *always* reported as grams per kilogram of sea water. It should be understood that the proposed system applies only to the *reporting* of analytical data in the literature. Any suitable units may be adopted for the *discussion* of special problems.

For expressing the amounts of the dissolved constituents, two types of units are proposed: (1) physical units of mass, volume, or pressure, and (2) units based upon the number of atoms of the designated element, which may be present as ions or molecules either singly or in combination with other elements. In certain cases the number of chemical equivalents is acceptable.

The mass units most commonly used are those of the metric system and bear the following relations to each other:

$$\begin{aligned} 1 \text{ ton} &= 10^3 \text{ kilograms (kg)} = 10^6 \text{ grams (g)} \\ 1 \text{ gram} &= 10^3 \text{ milligrams (mg)} = 10^6 \text{ mygrams } (\mu\text{g}) \end{aligned}$$

A measure of the number of atoms of the designated element is obtained by dividing the amount of the element, expressed as grams, milligrams, or mygrams, by the gram-atomic weight of the element. Hence,

$$\begin{aligned} 1 \text{ gram-atom (g-atom)} &= 10^3 \text{ milligram-atoms (mg-atoms)} \\ &= 10^6 \text{ mygram-atoms } (\mu\text{g-atoms}) \end{aligned}$$

Quantities expressed as gram-, milligram-, or mygram-atoms may be converted to the corresponding mass units by multiplying by the gram-atomic weight of the designated element.

In certain cases (for example, alkalinity and hydrogen-ion concentration) it is desirable to report the concentration in terms of chemical equivalents. The units shall then be

$$1 \text{ equivalent (val)} = 10^3 \text{ milli-equivalents (millival)}$$

For expressing the partial pressure of gases dissolved in sea water the basic pressure unit is the "physical atmosphere" (p. 55):

$$\begin{aligned} 1 \text{ physical atmosphere (atm)} &= 760 \text{ Torr} \\ &= 1.0133 \times 10^6 \text{ dynes/cm}^2 \\ &= 1.0133 \text{ bar} \end{aligned}$$

Partial pressures shall be expressed in Torr.

Volume units are all based upon the true liter—that is, the volume of 1 kg of distilled water at 4°C. When volume units are used, the temperature and pressure should be stated. The quantities of dissolved gases, when expressed as milliliters (ml), should be those for 0°C and a pressure of 1 atmosphere, that is, NTP.

The centigrade scale is to be used for reporting temperatures.

The units to be used in reporting data, proposed by the International Association of Physical Oceanography, are given in table 34. It should be noted that all units are based upon the amount of a designated element that may be present either singly (for example, oxygen or calcium) or in combination with other elements (for example, phosphate-phosphorus).

Because the 20° liter is the standard volume unit for expressing the quantity of sea water, glassware should be calibrated for this temperature, and, if practicable, measurements and chemical determinations should be made at or near this temperature. If the sea-water samples are not at 20°, it may be necessary to apply certain corrections. Full descriptions of the methods for making such corrections and tables to facilitate the transformation are included in the Report of the International Association of Physical Oceanography. In most cases the accuracy of the methods of analysis for the elements present in small amounts do not justify such corrections.

As already stated, it is frequently desirable to express the relative concentrations as Cl-ratios or chlorosity factors (p. 167). These relationships may be used to calculate the quantity of the major elements present in water of known chlorinity or to check variations in composition which may be brought about by natural agencies, pollution by sewage and industrial wastes, or by other agencies.

Composition of Sea Water

So far, the discussion of the composition of sea water has been based mainly on the results of the fundamental investigations of Dittmar. Since his time our knowledge of the composition of sea water has increased tremendously. Improved methods of analysis have been developed and consequently more accurate values can be obtained. Tests have also been developed for the detection and determination of elements other than those previously discussed. Particular efforts have been devoted to the study of the so-called plant nutrients—that is, those elements which are essential to plant growth in the sea but which are present in small and variable amounts. Individual elements have been studied both extensively and intensively, so that much more is now known concerning the regional differences in the ratios of the major constituents and in the amounts of the elements present in small quantities. However, except for Dittmar's work, there has been *no* careful study of the composition of a large number of samples for all the major constituents.

TABLE 34

ABBREVIATIONS AND UNITS TO BE USED IN REPORTING CHEMICAL DATA

(Scheme proposed by the International Association of Physical Oceanography)

Designated substance	Abbreviation	Units (p = preferred, a = alternative)			
		$\frac{\text{mg-atom}}{\text{L}}$	$\frac{\mu\text{g-atom}}{\text{L}}$	$\frac{\text{ml at NTP}}{\text{L}}$	$^0/_{00}$
Ammonia-nitrogen	Ammonia-N		p		
Argon	Argon	p			
Arsenate-arsenic	Arsenate-As		p		
Arsenite-arsenic	Arsenite-As		p		
Borate-boron	Borate-B	p			
Calcium	Ca	p			a
Carbon dioxide	Carbon dioxide-C	p			
	CO_2			a	
Chlorinity	Cl				p
Copper	Cu		p		
Iron	Fe		p		
Magnesium	Mg	p			a
Manganese	Mn		p		
Nitrate-nitrogen	Nitrate-N		p		
Nitrite-nitrogen	Nitrite-N		p		
Nitrogen (gas)	N_2	p		a	
Oxygen (gas)	O_2	p		a	
Phosphate-phosphorus	Phosphate-P		p		
Potassium	K	p			a
Radioactive substances					p
Salinity	S				p
Silicate-silicon	Silicate-Si		p		
Sodium	Na	p			a
Sulphate	Sulphate-S	p			
	SO_4				a
Hydrogen sulphide	Sulphide-S	p			
	H_2S			a	

Hence, in order to prepare a tabulation of the composition of sea water it is necessary to combine the results of numerous workers who have examined samples from different sources. All available data were collected by Thompson and Robinson (1932), and additional references will be found in the following discussion. In some cases the information is extensive, but for other elements only a few determinations have been made on water from a single locality. We shall first examine the quantities of the major elements—that is, those which bear a virtually constant relationship to the chlorinity.

In table 35 is given a compilation of the major ions that make up over 99.9 per cent of the known dissolved solid constituents of sea water. The sources of these data have been discussed by Lyman and Fleming (1940). The concentrations of the various ions are shown for water of 19.00 $^0/_{00}$ chlorinity, and also the Cl-ratios. The quantities are also expressed in terms of chemical equivalents per kilogram for water of 19.00 $^0/_{00}$ chlorinity and as milligram-atoms per 20° liter. Chlorosity factors are given for units of milligram-atoms. The carbon dioxide has been reported as bicarbonate. This method is not strictly accurate, because the bound carbon dioxide content of sea water is variable, but, as will be shown in the discussion of the carbon dioxide system, the sum of the chemical equivalents of carbonate and bicarbonate is virtually constant for any chlorinity.

It is immediately seen that the sum of the halides (chloride, bromide, and fluoride) by weight is greater than the chlorinity. The amount of iodide is negligible. Even if the bromide is calculated as chloride, and if the fluoride is disregarded because it does not take part in the chlorinity determination, the chloride equivalent is 1.00045 times greater than the chlorinity. The reasons for this apparent discrepancy have been discussed on page 52.

Lyman and Fleming (1940) obtained the following empirical equation for the dissolved solids as represented in table 35:

$$\Sigma\ ^0/_{00} = 0.073 + 1.8110\ \text{Cl}\ ^0/_{00}.$$

From this it will be seen that in water of 19.00 $^0/_{00}$ chlorinity the *total dissolved* solids are 34.4816 $^0/_{00}$, but, according to the equation used to calculate the salinity from the chlorinity (p. 51), the salinity is 34.325 $^0/_{00}$. Thus, the total amount of dissolved solids is greater than the salinity. If, on the other hand, the salinity is calculated from the total solids, using the definition for the former quantity—that is, by converting the bicarbonate to oxide and converting the bromide to chloride—we obtain the salinity "by definition" as 34.324 $^0/_{00}$. This agreement must be considered as more or less accidental, as there are many uncertainties in the analytical data. Confidence in the values is strengthened, however, by the fact that the sodium:chlorinity ratio as reported by Robinson

TABLE 35
MAJOR CONSTITUENTS OF SEA WATER
(Cl = 19.00 ‰, ρ_{20} = 1.0243)

Ion	‰	Cl-ratio, g per unit Cl	Equivalent per kg of sea water	mg-atoms per liter	Chlorosity factor, mg-atoms per unit *Cl*	Authority
Chloride, Cl^-	18.9799	0.99894	0.5353	548.30	28.17_3	Dittmar (1884), Jacobsen and Knudsen (1940)
Sulphate, $SO_4^{=}$	2.6486	0.1394	0.0551	(SO_4-S) 38.24	1.45_1	Thompson, Johnston, and Wirth (1931)
Bicarbonate, HCO_3^-	0.1397	0.00735[a]	0.0023	(HCO_3-C) 2.34	0.12_0	Revelle (1936)
Bromide, Br^-	0.0646	0.00340	0.0008	0.83	0.042_6	Dittmar (1884)
Fluoride, F^-	0.0013	0.00007	0.0001	0.07	0.003_6	Thompson and Taylor (1933)
Boric acid,[c] H_3BO_3	0.0260	0.00137[b]	[c]	(H_3BO_3-B)0.43	0.022_1	Harding and Moberg (1934), Igelsrud, Thompson, and Zwicker (1938)
Total			0.5936			
Sodium,[d] Na^+	10.5561	0.5556	0.4590	470.15	24.15_8	By difference, and Robinson and Knapman (1941)
Magnesium, Mg^{++}	1.2720	0.06695	0.1046	53.57	2.75_2	Thompson and Wright (1930)
Calcium, Ca^{++}	0.4001	0.02106	0.0200	10.24	0.526_2	Kirk and Moberg (1933); Thompson and Wright (1930)
Potassium, K^+	0.3800	0.02000	0.0097	9.96	0.511_8	Thompson and Robinson (1932)
Strontium, Sr^{++}	0.0133	0.00070	0.0003	0.15	0.007_7	Webb (1938)
Total			0.5936			

Total dissolved solids = 34.4816 ‰
Sum of constituents (HCO_3^- as $O^=$, and Br^- as Cl^-) = 34.324 ‰
Salinity (S ‰ = 0.030 + 1.805 Cl ‰) = 34.325 ‰

[a] Ratio for millival/kg = 0.1205

[b] Ratio for boron/Cl = 0.000240

[c] Boric acid undissociated

[d] Sodium calculated by difference in sums of equivalents

and Knapman (1941) agrees exactly with the value that Lyman and Fleming (1940) found by difference. Although the table represents the most probable figures for the composition of the major dissolved constituents, it is subject to change as additional data become available.

The data in table 35 apply more specifically to surface water than to deep water. Both bicarbonate ion and calcium will be slightly higher in deeper water. Furthermore, some of the other compounds not included in this tabulation, such as nitrate and silicate, may be present in sufficient quantities to disturb the balance of the anions and cations shown in the table. The Cl-ratios should therefore be considered more as indices than as absolute values. However, in no case will the ratios vary by more than a unit or two in the last decimal place when the water under investigation is from the open sea. Under abnormal conditions, as in highly diluted water, larger departures may be found. By definition the salinity is not zero at zero chlorinity; hence the ratios of certain elements would be expected to approach infinity at very high dilutions when the diluting water contained substances other than halides. Therefore, in studies in areas of highly diluted water the character of the river water should be taken into account. As pollution problems frequently occur in such areas, it will be necessary to determine the normal ratios for different dilutions for a specific zone before any conclusions can be drawn as to the nature or extent of the pollution.

Elements Present in Sea Water

Thus far, only the major constituents of sea water have been considered. In table 36 are entered all elements that are known to occur in sea water as dissolved solids, except hydrogen and oxygen. They are not given as ions in this case but as the amounts of the individual elements which occur in water of chlorinity 19.00 $^0/_{00}$. The elements are arranged in the order of their abundance. In the first column they are reported as milligrams per kilogram, and in the second as milligram-atoms per liter. For convenience, the 1940 atomic weights and their reciprocals have been included. These constants are necessary when converting weight units to gram-atom units, and vice versa. The values for the major elements correspond to those given in previous tables and, in general, are valid for surface water. For many of the elements ranges in concentration have been indicated. No doubt ranges should be shown for others, but the lack of sufficient observations or uncertainty as to the reliability of reported data leaves these problems unsettled. For many of the elements that are present in very low concentrations there are only one or two determinations available, and in some cases only indirect estimates have been made. Hence, in these cases the indicated values can represent only the order of magnitude of the quantities present. Omitting the six most abundant elements, only carbon (CO_2 components), silicon, nitrogen, and phosphorus compounds have been studied with sufficient completeness to provide a fairly good idea of their distribution. Less complete studies have been made on the variations in the amounts of boron, iodine, iron, manganese, copper, gold, and radium. Cadmium, chromium, cobalt, and tin have been found in the ash of marine organisms, and hence it is implied that they occur in sea water, although so far they have not been shown directly.

Forty-four elements are listed in table 36, and if we add hydrogen, oxygen, and the inert gases neon, helium, and argon, we obtain a total of forty-nine elements that are known to occur in sea water. Further investigations will undoubtedly demonstrate the presence of others. Certain problems of the origin and concentration of the dissolved solids relative to their concentration in the earth's crust will be discussed later.

The following brief discussion is limited to those elements that either occur in relatively large amounts or whose distribution has been shown to be affected by biological activity. For elements in the latter group additional data are given in chapter VII. In table 36 references are given for those elements not discussed in the text. A comprehensive discussion is given by Thompson and Robinson (1932), and other results are reported by Goldschmidt (1937) and Wattenberg (1938). The elements are considered in the order in which they appear in the table.

Chlorine, present as chloride ion, is the most abundant ion and makes up about 55 per cent by weight of the dissolved material. It is rarely measured except in combination with other halides in the chlorinity determination. The bromide and iodide are then computed as if they were chloride. It should be kept in mind that the ratio of the chlorine-equivalent of the halides to the chlorinity is 1.00045 (p. 52). The chlorinity is of the greatest importance, not only as the basis of density computations, but also as the standard to which those substances present in major amounts are referred.

Sodium is the most abundant cation in sea water, but it is rarely determined directly, owing to the technical difficulties involved in the determination of the alkali metals. The average ratio to chlorinity, 0.5556, as obtained by Robinson and Knapman (1941) agrees exactly with the value that Lyman and Fleming (1940) calculated by difference. It is somewhat higher than the average of 0.5509 given by Thompson and Robinson (1932), but is in fair agreement with the ratio 0.5549 obtained by Webb (1939) by direct analysis. The sodium: chlorinity ratio may be modified near river mouths.

Magnesium content of sea water has been investigated rather carefully, particularly by Thompson and Wright (1930). The magnesium is usually determined by a special modification of the magnesium-ammonium-phosphate method. The ratio of magnesium to chlorinity is very uniform.

TABLE 36
ELEMENTS PRESENT IN SOLUTION IN SEA WATER
(Dissolved gases not included)

Element	mg/kg Cl = 19.00 ‰	mg-atoms/L Cl = 19.00 ‰	Atomic weight (1940)	1/atomic weight	Authority
Chlorine	18980	548.30	35.457	0.02820	
Sodium	10561	470.15	22.997	0.04348	
Magnesium	1272	53.57	24.32	0.04112	
Sulphur	884	28.24	32.06	0.03119	
Calcium	400	10.24	40.08	0.02495	
Potassium	380	9.96	39.096	0.02558	
Bromine	65	0.83	79.916	0.01251	
Carbon	28	2.34	12.01	0.08326	
Strontium	13	0.15	87.63	0.01141	
Boron	4.6	0.43	10.82	0.09242	
Silicon	0.02 –4.0	0.0007 –0.14	28.06	0.03564	
Fluorine	1.4	0.07	19.00	0.05263	
Nitrogen (comp.)	0.01 –0.7	0.001 –0.05	14.008	0.07139	
Aluminum	0.5	0.02	26.97	0.03708	
Rubidium	0.2	0.002	85.48	0.01170	
Lithium	0.1	0.014	6.940	0.14409	
Phosphorus	0.001–0.10	0.00003–0.003	30.98	0.03228	
Barium	0.05	0.0004	137.36	0.00728	
Iodine	0.05	0.0004	126.92	0.00788	
Arsenic	0.01 –0.02	0.00015–0.0003	74.91	0.01335	
Iron	0.002–0.02	0.00003–0.0003	55.85	0.01791	
Manganese	0.001–0.01	0.00002–0.0002	54.93	0.01820	
Copper	0.001–0.01	0.00002–0.0002	63.57	0.01573	
Zinc	0.005	0.00008	65.38	0.01530	Atkins (1936)
Lead	0.004	0.00002	207.21	0.00483	Boury (1938)
Selenium	0.004	0.00005	78.96	0.01266	Goldschmidt and Strock (1935)

TABLE 36 (*Continued*)

Element	mg/kg Cl = 19.00 $^{0}/_{00}$	mg-atoms/L Cl = 19.00 $^{0}/_{00}$	Atomic weight (1940)	1/atomic weight	Authority
Cesium	0.002	0.00002	132.91	0.00752	Wattenberg (1938)
Uranium	0.0015	0.00001	238.07	0.00420	Föyn *et al* (1939)
Molybdenum	0.0005	0.000005	95.95	0.01042	Ernst and Hoermann (1936)
Thorium	<0.0005	<0.000002	232.12	0.00431	Föyn *et al* (1939)
Cerium	0.0004	0.000003	140.13	0.00714	Goldschmidt (1937)
Silver	0.0003	0.000003	107.880	0.00927	Haber (1928)
Vanadium	0.0003	0.000006	50.95	0.01963	Ernst and Hoermann (1936)
Lanthanum	0.0003	0.000002	138.92	0.00720	Goldschmidt (1937)
Yttrium	0.0003	0.000003	88.92	0.01125	Goldschmidt (1937)
Nickel	0.0001	0.000002	58.69	0.01704	Ernst and Hoermann (1936)
Scandium	0.00004	0.0000009	45.10	0.02217	Goldschmidt (1937)
Mercury	0.00003	0.0000001	200.61	0.00498	Goldschmidt (1937)
Gold	0.000006	0.00000002	197.2	0.00507	Haber (1928)
Radium	$0.2 - 3 \times 10^{-10}$	$0.8 - 12 \times 10^{-13}$	226.05	0.00442	Evans, Kip, and Moberg (1938)
Cadmium					Fox and Ramage (1931)
Chromium					Webb (1937)
Cobalt					Thompson and Robinson (1932)
Tin					Thompson and Robinson (1932)

Sulphur is present in sea water as sulphate ion, and is in this form usually determined by precipitation as barium sulphate. An extensive study of the sulphate distribution has been made by Thompson, Johnston, and Wirth (1931). Under stagnant conditions occurring in certain isolated basins, and in and near bottom sediments, a part of the sulphate may be converted to sulphide ion. Considerable quantities of sulphide occur in the Black Sea and in certain Norwegian fjords, and its presence has been reported in many localities. The sulphate:chlorinity ratio may also be modified by dilution with river water, which is generally relatively high in sulphate. Processes of freezing and melting may possibly affect the relative concentration (p. 216).

Calcium is present in much smaller quantities than either sodium or magnesium, but its distribution in the ocean has been studied much more thoroughly, mainly because calcium is a major constituent of many skeletal remains found in marine sediments. By deposition of such remains calcium is permanently removed from the water, but this removal does not necessarily imply that the calcium concentration is decreasing, because a large supply is maintained by the river waters flowing into the sea. Detectable differences in the calcium:chlorinity ratio have been observed. In the Baltic, Gripenberg (1937a) has shown that the type of river water which has diluted the sea water can be determined from that ratio. Furthermore, Moberg and Revelle (1937) have demonstrated the existence of vertical differences in the calcium: chlorinity ratio which they attribute to the removal of calcium in the surface layers through biological activity. Interest in the concentration of calcium has also centered around the question of the solubility of calcium carbonate in sea water and the factors that control precipitation and solution. In certain areas calcium carbonate is apparently precipitated inorganically, and in other regions it apparently passes into solution. In addition to these problems, knowledge of the calcium concentration is important in an understanding of the carbon dioxide system in the sea, which will be discussed later. The quantity of calcium is usually determined by precipitation as the oxalate under carefully controlled conditions and subsequent titration with potassium permanganate. One such method has been described by Kirk and Moberg (1933).

Webb has pointed out that in this method for the estimation of calcium the strontium will be carried down, and hence the calcium figure will be too high by the equivalent amount of strontium. As the ratio calcium:strontium is apparently constant, Webb suggests that the "calcium" shall be taken to mean the calcium after the strontium and barium have been replaced by calcium. Since the barium is negligible in this case, the values of "calcium" will be given directly by volumetric methods, but when the quantities are determined by weighing, corrections must be applied (Webb, 1938). Values cited in this discussion are for calcium alone and have been obtained by correcting the analytical data for the presence of strontium. The "calcium" Cl-ratio as defined by Webb and corresponding to the values of calcium and strontium in table 35 is 0.0214.

Potassium is the fourth most abundant cation and is present in amounts of only a few per cent of that of sodium. The potassium is rarely determined directly, but apparently it bears a very constant relationship to the chlorinity (Thompson and Robinson, 1932). However, the content of potassium may be modified by biological agencies, since some organisms, particularly the large algae, concentrate potassium to a marked degree. The ratio of the potassium to chlorinity may also be modified by dilution with river water. The potassium may react with the colloidal and clay particles brought to the sea by rivers and run-off, and consequently this agency may influence the ratio. Certain minerals formed on the sea bottom, such as glauconite, contain potassium.

Bromine shows a very constant ratio to the chlorinity and is apparently all present as bromide ion.

Discussion of the concentration of *carbon* in sea water is complicated by the fact that it occurs not only in the form of carbonic acid and its salts but also in appreciable amounts as a constituent of organic material, either living or dead. The detrital organic material may be either particulate or in solution. The solubility of carbon dioxide depends upon the temperature and salinity of the water, and exchange of carbon dioxide with the atmosphere takes place at the surface. Photosynthesis in the surface layers reduces the amount of carbon dioxide in the water, and respiration increases the concentration. Consequently, the quantities of carbon present as either free carbon dioxide, bicarbonate, or carbonate will show a considerable range. These problems will be discussed in the sections dealing with the carbon dioxide system in the sea. The quantity of carbon given in table 36 was calculated on the assumption that only bicarbonate ions were present. The organic carbon, which is probably of the order of 2 to 3 mg/L (0.15 to 0.25 mg-atoms/L), was not included. The methods by which the different carbon dioxide components and the particulate and dissolved organic carbon may be determined are discussed later.

Strontium has not been investigated in detail, as it is extremely difficult to determine quantitatively. In determinations of calcium by means of the oxalate precipitation, the strontium is carried down with the calcium, and consequently the ratio of calcium:chlorinity usually reported for sea water represents the calcium plus strontium reported as calcium. Strontium is a constituent of the calcareous skeletons of certain organisms.

Boron occurs in sea water in a surprisingly high concentration and bears a constant relationship to the chlorinity. Apparently it is present as undissociated boric acid. There has been considerable uncertainty as to the form in which boron occurs, but the method of determination is standardized against boric acid and the values can at least be expressed as equivalent to a certain concentration of boric acid. The determination of boric acid in sea water is based on titration with very dilute sodium hydroxide in the presence of mannitol. Methods have been described by Harding and Moberg (1934) and by Igelsrud, Thompson, and Zwicker (1938). The amount of boron present in sea water is of interest in the carbonate equilibria and in this connection will be discussed later. Boron is concentrated by certain marine organisms.

Silicon has been studied extensively because it is utilized by diatoms and other silica-secreting organisms. According to a tabulation by Thompson and Robinson (1932), the silicate-silicon varies by more than one hundredfold—namely, from 0.0007 to 0.11 mg-atoms/L (0.02 to 3.0 mg/L). Clowes (1938) found values slightly exceeding .14 mg-atoms/L (4.0 mg/L) in the deep waters of the Antarctic. Surface samples are usually low, owing to the development of silica-secreting organisms, but a progressive increase in silicate takes place with depth, which is ascribed to the dissolving of soluble silicates. However, there is always the possibility that the water contains silicon in some compound present in colloidal form. River water contains a high content of silicon, both in solution and as colloidal particles. Diatom and radiolarian oozes contain the siliceous remains of organisms that have developed near the surface and settled to the bottom after their death. Although siliceous deposits of organic origin cover large areas, most of the siliceous skeletal remains dissolve after the death of the organisms. Silicon present as soluble silicate is determined colorimetrically. The method has been described by Thompson and Houlton (1933) and by Wattenberg (1937). Because of the rapidity with which water samples are contaminated by silicate that dissolves from the glass, the analyses should be made soon after the water samples are collected. Waxed containers are sometimes recommended, and it is always desirable to use "aged" bottles that have been thoroughly leached with sea water. Tourky and Bangham (1936) tested the reaction between the molybdate reagent and colloidal silica and found that the color development was not proportional to the amount of silicon present. Treatment of the colloidal silica with alkali prior to analysis yielded correct values. Experiments with sea water indicated that colloidal silica may pass into true solution on ageing.

Fluorine is present in oceanic sea water in concentrations slightly above 1 mg/L. It is present as fluoride and, according to the work of Thompson and Taylor (1933), bears a constant ratio to the chlorinity.

The method of determination is described by these authors. Little is known concerning the role of fluorine in the sea.

Nitrogen occurs in sea water both in compounds of various kinds and as free dissolved nitrogen gas. As it is an essential constituent of living matter, nitrogen is found in organic compounds both in organisms and in particulate and dissolved organic material in amounts between 0.1 and 10.0 μg-atoms/L (p. 254). In addition, it is present as nitrate, nitrite, and ammonia. In routine observations only the inorganic nitrogen compounds are determined. Nitrate- and nitrite-nitrogen are determined colorimetrically, and the ammonia either colorimetrically (Robinson and Wirth, 1934) or by micro-titration after distillation (Krogh, 1934).

The nitrate method originally described by Harvey (1926) is given by Wattenberg (1937). Rakestraw (1936) and Wattenberg describe the procedure for the determination of nitrite. Since the inorganic nitrogen compounds are subject to change after the water samples have been collected, analyses must be run within a few hours. Even the addition of preservatives may not prevent changes in the NH_3 and NO_2, indicating that purely chemical transformations may be involved. Ammonia tends to disappear in storage, and nitrite sometimes decreases, but at other times shows an increase. The nitrate, which is more abundant, does not show such relatively large changes.

Because of their relatively low concentrations and their utilization by organisms, the inorganic nitrogen compounds show a wide range in values:

Nitrate-N	0.1–43.0 μg-atoms/L, 1–600 μg/L
Nitrite-N	0.01–3.5 μg-atoms/L, 0.1–50 μg/L
Ammonia-N	0.35–3.5 μg-atoms/L, 5–50 μg/L

The distribution of nitrate in the oceans has been and is studied a great deal, as it may limit the production of phytoplankton when it is reduced to minimal quantities in the surface layers. Nitrate-nitrogen usually shows a subsurface maximum at a depth of several hundred meters. Nitrite nitrogen has a peculiar distribution and is generally found in a rather thin stratum in or above the thermocline. Less is known concerning the distribution of ammonia, as it is not so readily measured as the other inorganic compounds of nitrogen, but it is apparently rather uniform throughout the water column.

Nitrogen compounds are carried to the sea by rivers and by precipitation. The greater part of these are supposed to have been fixed by electrical discharges in the atmosphere. Possibly a certain amount of the fixed nitrogen in the sea is liberated as free nitrogen and returned to the atmosphere. Bottom sediments contain a small percentage of organic nitrogen in resistant organic detritus, and a part of this is permanently lost from the water, as it is found in all types of sediments, both recent and fossil. As the carbon:nitrogen ratio in organic material is relatively constant, the organic nitrogen is frequently used as a measure of the amount of organic matter in marine sediments and also in the water. The distribution of nitrogen compounds and the nitrogen cycle in the sea are discussed in chapters VII and XVIII.

Aluminum is present in sea water in very small amounts. The colloidal clay particles which are carried to the sea contain a large percentage of aluminum, and hence analyses of water samples collected near shore may show the presence of aluminum, but it is not necessarily all in solution. The value given in table 36 is the average quantity reported by Haendler and Thompson (1939). Their values range between 0.006 and 0.065 mg-atoms/L (0.16 and 1.8 mg/L) with an average of 0.02 mg-atoms/L (0.54 mg/L).

Although earlier workers (Thompson and Robinson, 1932) were unable to detect *rubidium* in sea water, Goldschmidt (1937) has reported about 0.002 mg-atoms/L (0.2 mg/L).

Lithium content of sea water has been investigated by Thomas and Thompson (1933), who found 0.014 mg-atoms/L (0.1 mg/L).

Phosphorus, which is present in sea water as phosphate ions, is another of the essential constituents of living organisms, and its distribution in the sea is markedly affected by organic agencies. In addition to the nitrogen and silicon compounds, phosphate-phosphorus has been considered as one of the substances that may limit production of plant life. The inorganic phosphorus concentration varies from virtually zero at the surface, under certain conditions, to approximately 0.003 mg-atoms/L (0.090 mg/L) at subsurface levels when values are corrected for salt error. There is frequently a subsurface maximum similar to that in the distribution of nitrate-nitrogen. Phosphorus removed from the surface layers by phytoplankton is largely returned to solution on the death and decomposition of the organisms. It is supplied by rivers, and some is removed from the sea, as a small quantity is present in most marine sediments. In certain shallow areas, phosphatic concretions are found that contains a rather high concentration of phosphorus. The mode of origin of these concretions is not yet known. It has been suggested that in many regions the water is supersaturated in respect to tricalcium phosphate which, therefore, may be deposited inorganically (Dietz, Emery, and Shepard, 1942).

Phosphate phosphorus is determined colorimetrically. The method has been described by Robinson and Wirth (1935) and Wattenberg (1937). Cooper (1938a) has discussed the magnitude of the salt error. Phosphate analyses are frequently carried out as routine observations, and our knowledge of the distribution of phosphate in the ocean is fairly comprehensive. The rather scant knowledge we have concerning the amount of phosphorus present as particulate or dissolved organic phosphorus will be discussed in connection with the phosphorus cycle in the sea (chapter VII).

The amount of *barium* in sea water has been reported by Goldschmidt (1937) as 0.0004 mg-atoms/L (0.05 mg/L). This is lower than the values reported by Thompson and Robinson (1932). Barium occurs in marine organisms and it is a constituent of most marine sediments. In certain localities the deposits contain large amounts of barium sulphate in the form of concretions and nodules. The mode of formation of these structures is not yet understood.

The distribution and concentration of *iodine* in the sea has received a great deal of attention because of its important role in the physiology of man and terrestrial animals. Marine products are an important source of iodine-rich foods. The form in which iodine occurs in sea water is not yet clearly understood, but at least part of it is present as iodide and iodate. It is concentrated to a marked degree by marine plants, and for many years sea weeds have been used as a commercial source of iodine. The distribution and determination of iodine in sea water and marine organisms have been discussed by Closs (1931) and Reith (1930).

Arsenic content of sea water has been investigated by Rakestraw and Lutz (1933), who report values ranging from 0.15 to 0.3 μg-atoms/L (9 to 22 μg/L). This wide range is attributed to the fact that organisms may utilize arsenic in place of phosphorus. It is known to be a constituent of the tissues of many marine forms. The exact form in which arsenic occurs in sea water is not yet known.

Iron is an essential constituent of plants and has been considered as one of the substances that may limit the amount of plant production in the sea. Investigations show that at least part of the iron is not present in true solution, as it can be removed by ultrafiltration. Cooper (1937b) has pointed out that the amount of iron in true solution as ferric or ferrous salts is probably less than 2 μg/L, whereas the total iron present is generally about ten times this quantity. The amount present in the plankton may be as much as 16 per cent of the total iron of the water. Harvey (1937) considers that diatoms are able to adsorb and utilize colloidal iron. Iron is brought to the sea in relatively large quantities in the colloidal clay particles, and consequently considerable amounts of iron are found in the marine sediments. In many instances the iron content of the sediments is even higher than should be expected, indicating addition of iron through physical, chemical, or organic agencies. In inshore areas near the source of supply the total iron content of the water is sometimes much higher than that found in the open ocean. Methods for the determination of iron in sea water in its various forms have been described by Thompson and Bremner (1935a and b), Cooper (1935), and Rakestraw, Mahnke, and Beach (1936).

Manganese is apparently subject to concentration by marine organisms. Thompson and Wilson (1935) have reported values between 0.02 and 0.2 mg-atoms/L (1 and 10 mg/L). The value cited by Goldschmidt (1937) is 4 mg/L. Interest in manganese has been aroused by the occurrence of manganese nodules which are widely distributed in certain types of marine sediments, particularly in the Pacific Ocean.

The quantity of *copper* present in sea water probably lies between 0.02 and 0.2 μg-atoms/L (1 to 10 μg/L) (Marks, 1938, Wattenberg, 1938). Copper is an essential constituent of many marine organisms and it is also considered a factor in the life history of oysters, as a relatively high copper content of the water is apparently necessary for proper development of the larvae.

Much interest is attached to the content of *radioactive elements* in sea water, because deep-sea sediments are high in radium, compared to igneous rocks, and it is considered that the enrichment must be due to precipitation from the water of radium or its precursors. The *radium* content of sea water has been studied by many investigators, using various techniques, but it is only recently that methods have been sufficiently refined to yield trustworthy results. Studies by Evans, Kip, and Moberg (1938) and by Pettersson and Rona (Föyn *et al*, 1939) show that the radium content, measured by the radon emanation technique, varies between about 0.2 and 3.0×10^{-13} $^0/_{00}$ in sea water of salinity approximately 35 $^0/_{00}$. The low values are found in the surface layers, and it is suggested that organisms are responsible for a selective removal of this element. Both groups of workers found that organisms concentrate the radium about one hundredfold in their soft tissues. Calcareous structures show an increase in the radium:calcium ratio over that in the water. The maximum value listed above—namely 3.0×10^{-13} $^0/_{00}$—was found in water in contact with the sediments (Evans, Kip, and Moberg, 1938), and generally the radium content of the deeper waters is about 1×10^{-13} $^0/_{00}$.

Pettersson and co-workers (Föyn *et al*, 1939) have emphasized the importance of searching for the radioactive precursors of radium, as this element has the relatively short half-life period of only 1690 years. Of these elements uranium and ionium are probably the most important, but thus far only *uranium* has been examined. Karlik (Föyn *et al*) has analyzed a number of samples from various parts of the oceans and obtained for oceanic water a mean value of 1.5×10^{-6} $^0/_{00}$. Surface waters have a somewhat lower content than those from greater depths, but Karlik does not consider that the data are sufficiently adequate to show any differential removal. Studies of the dilute waters of the Baltic Sea showed that the uranium content was a function of the salinity.

Föyn and Rona (Föyn *et al*) have sought for *thorium* in sea water, but have been unable to detect it by the most refined methods. By examining very large samples they have fixed an upper limit of 0.5×10^{-6} $^0/_{00}$ for this element. Older and apparently less accurate methods yielded considerably higher values.

The radium content of marine sediments and the theories concerning the deposition of radium and its precursors are discussed in the chapter on marine sedimentation.

Preparation of Artificial Sea Water

It is impossible to prepare solutions that exactly duplicate the properties of sea water because (1) the ions (salts) in which the elements occur in sea water are not always known, (2) elements that occur in sea water in small amounts are present as contaminants in other compounds in quantities which may far exceed those that should be added, and (3) many of the salts which must be added in fairly large amounts are hygroscopic or contain water of crystallization and are difficult to weigh accurately. The latter difficulty may be partially avoided by preparing concentrated solutions of these salts, determining their concentration by chemical analysis, and adding the required volume of the solution.

Although it would be of great interest to prepare solutions duplicating all the physical and chemical properties of sea water, it is generally not essential. In studies of certain of the physical-chemical properties, it is sufficient to add to the solution only the more abundant ions. In other instances—for example, when chemical methods are to be standardized—only one element or ion need be accurately known and other ions only approximately. Furthermore, in experiments with marine plants the major elements may not have to be closely controlled, but it will generally be necessary to know the concentrations of the biologically essential elements that are normally present in small amounts. If possible, natural sea water should always be used in physical or biological studies, but in the latter case it is sometimes desirable to enrich the water with certain of the plant nutrients (p. 235). Rogers (1938) has discussed various "modified" types of solutions that are used in experiments on marine animals.

In table 37 are given three suggested formulae for preparing solutions approximating the composition of sea water. They have been adjusted to yield solutions of 19.00 $^0/_{00}$ chlorinity. The recipe of McClendon *et al* (1917), which has been used quite extensively, contains the nitrogen, phosphorus, and silicon needed by marine plants. Additional elements may be necessary but are probably always present as impurities. The formulae of Brujewicz (Subow, 1931) and of Lyman and Fleming (1940) contain only the major elements. The last-mentioned recipe corresponds to the composition of sea water given in table 35. The other formulae have not been adjusted to the composition presented in earlier sections of this chapter. In all cases the reagents used should be examined for contaminants and, if necessary, purified.

TABLE 37
FORMULAE FOR ARTIFICIAL SEA WATER
(Cl = 19.00 ‰)

McClendon *et al* (1917)		Brujewicz (Subow, 1931)		Lyman and Fleming (1940)	
Salt	g/kg	Salt	g/kg	Salt	g/kg
NaCl	26.726	NaCl	26.518	NaCl	23.476
$MgCl_2$	2.260	$MgCl_2$	2.447	$MgCl_2$	4.981
$MgSO_4$	3.248	$MgSO_4$	3.305	Na_2SO_4	3.917
$CaCl_2$	1.153	$CaCl_2$	1.141	$CaCl_2$	1.102
KCl	0.721	KCl	0.725	KCl	0.664
$NaHCO_3$	0.198	$NaHCO_3$	0.202	$NaHCO_3$	0.192
NaBr	0.058	NaBr	0.083	KBr	0.096
H_3BO_3	0.058			H_3BO_3	0.026
Na_2SiO_3	0.0024			$SrCl_2$	0.024
$Na_2Si_4O_9$	0.0015			NaF	0.003
H_3PO_4	0.0002				
Al_2Cl_6	0.013				
NH_3	0.002				
$LiNO_3$	0.0013				
Total	34.4406		34.421		34.481
Water to	1,000.0000	Water to	1,000.000	Water to	1,000.000

Dissolved Gases in Sea Water

All of the atmospheric gases are found in solution in sea water. In addition to nitrogen and oxygen, the most abundant gases in the air, carbon dioxide is present in large quantities in sea water, chiefly combined as carbonates and bicarbonates. Of the rarer gases, ammonia, argon, helium, and neon have been reported in sea water, and hydrogen is undoubtedly present in minute quantities. In the absence of dissolved oxygen, hydrogen sulphide may be present, and it is possible that in stagnating water other products of putrefactive decomposition, such as methane, may occur.

Because of its importance in biological processes the dissolved oxygen distribution in the oceans has been examined intensively. Besides being an index to the biological history of the water, the general character of the distribution of oxygen in the deeper water is helpful in studies of currents and of mixing processes. The carbon dioxide distribution is of equal biological importance; its discussion begins on p. 192. Nitrogen has not been studied very widely, as it is apparently chemically inert. Argon is also inert, and is sometimes included with the nitrogen when the dissolved gases are determined gasometrically. The presence of helium and neon has been confirmed by Rakestraw, Herrick, and Urry (1939).

DETERMINATION OF DISSOLVED GASES. The content of dissolved oxygen is usually determined by the Winkler method, which depends upon the oxidation of manganous hydroxide by the dissolved oxygen. When acid is added, the oxidized manganese reacts with potassium iodide and sets free iodine, in amounts equivalent to the original dissolved oxygen content, which is determined by titration with sodium thiosulphate. The Winkler method is simple and extremely accurate if certain precautions are observed in handling the water samples and reagents (Thompson and Robinson, 1939).

Problems relating to the determination of carbon dioxide are discussed on p. 192.

Dissolved nitrogen cannot be determined by direct chemical methods, and hence gasometric techniques must be used. In general, the sea-water sample is acidified and all the gases are driven off by boiling or by applying a vacuum. The carbon dioxide is then absorbed in alkali, and the oxygen is absorbed in alkaline pyrogallol. The residual gas is sometimes considered as "atmospheric nitrogen," although actually there are other gases, principally argon, mixed with it. Rakestraw and Emmel (1937) developed a method for determining the dissolved oxygen and nitrogen content of sea water by first extracting the gases and removing the carbon dioxide, then absorbing the oxygen on phosphorus and the nitrogen on molten lithium. The oxygen contents determined in this way agreed with direct Winkler analyses. The nitrogen determinations on saturated water samples showed results consistently lower than the saturation values according to Fox (1907); further studies (Rakestraw and Emmel, 1938b) indicate that Fox's tables are slightly in error. The gases remaining after the extraction of nitrogen are considered as "argon."

The presence of hydrogen sulphide can be detected by its characteristic odor. A method for its determination has been described by Gaarder (1916). Although commonly referred to as hydrogen sulphide, a part, at least, will not be present as free gas but as sulphide or bisulphide of some base. A hydrogen sulphide system somewhat comparable to the carbon dioxide system must exist, but it has not yet been investigated.

The determination of ammonia is discussed in the section dealing with nitrogen compounds.

The units to be used in reporting the concentrations of dissolved gases are mg-atoms/L or (ml of gas at NTP)/L.

In some cases it is of interest to know the excess or deficiency of the concentration with respect to water of the same temperature and salinity in equilibrium with the normal dry atmosphere. The saturation values for oxygen and nitrogen are given in tables 38 and 39. If the saturation values are known, the percentage saturation may be calculated. In certain problems it is desirable to know the partial pressures of the gases dissolved in a given water sample. The factors for computing these values are discussed on p. 190.

TABLE 38
SATURATION VALUES OF OXYGEN IN SEA WATER (ml/L)* FROM NORMAL DRY ATMOSPHERE
(Fox, 1907)

Chlorinity ($^0/_{00}$)	15	16	17	18	19	20
Salinity ($^0/_{00}$) / Temperature (°C)	27.11	28.91	30.72	32.52	34.33	36.11
−2	9.01	8.89	8.76	8.64	8.52	8.39
0	8.55	8.43	8.32	8.20	8.08	7.97
5	7.56	7.46	7.36	7.26	7.16	7.07
10	6.77	6.69	6.60	6.52	6.44	6.35
15	6.14	6.07	6.00	5.93	5.86	5.79
20	5.63	5.56	5.50	5.44	5.38	5.31
25	5.17	5.12	5.06	5.00	4.95	4.86
30	4.74	4.68	4.63	4.58	4.52	4.46

* mg-atoms of oxygen per liter = 0.08931 × ml/L.

TABLE 39
SATURATION VALUES OF NITROGEN IN SEA WATER (ml/L)* FROM NORMAL DRY ATMOSPHERE
(Rakestraw and Emmel, 1938b)

Chlorinity ($^0/_{00}$)	15	16	17	18	19	20	21
Salinity ($^0/_{00}$) / Temperature (°C)	27.11	28.91	30.72	32.52	34.33	36.13	37.94
0	15.22	15.02	14.82	14.61	14.40	14.21	14.01
5	13.43	13.26	13.10	12.94	12.78	12.62	12.45
10	12.15	12.00	11.86	11.71	11.56	11.42	11.27
15	11.04	10.92	10.79	10.66	10.53	10.39	10.26
20	10.08	9.98	9.87	9.76	9.65	9.54	9.43
25	9.30	9.21	9.11	9.02	8.92	8.82	8.73
28	8.89	8.84	8.72	8.62	8.53	8.44	8.35

* mg-atoms of nitrogen per liter = 0.08929 × ml/L.

The dissolved oxygen in the sea varies between zero and 0.75 mg-atoms/L (about 8.5 ml/L), although in areas of low temperature and intense photosynthesis the content may exceed this upper limit. Nitrogen, which is apparently unaffected by biological processes, varies between 0.75 and 1.3 mg-atoms/L (8.4 and 14.5 ml/L). The total carbon dioxide in oceanic waters varies between about 1.5 and 2.5 mg-atoms of C/L (34 and 56 ml/L). "Argon" varies between 0.2 and 0.4 ml/L, and the content of helium and neon in sea water is about 1.7×10^{-4} ml/L. The latter values apparently represent the saturation values. Hydrogen sulphide, which is present in the water under exceptional conditions, may occur in amounts of more than 1.0 mg-atom of S/L (22 ml/L) (Ström, 1936).

Factors Controlling the Distribution of Dissolved Gases. The following general factors control the distribution of dissolved gases in the oceans: (1) temperature and salinity, which determine the concentrations when the water is at the surface and in equilibrium with the atmosphere, (2) biological activity, which markedly affects the concentrations of oxygen and carbon dioxide, (3) currents and mixing processes, which tend to modify the effects of biological activity through mass movement and eddy diffusion.

Water in contact with the atmosphere will tend to reach equilibrium either by giving up or absorbing the individual gases until the water is just saturated. Although the zone of contact is a thin one, convective movements due to cooling, evaporation, or wind action may bring a layer of considerable thickness into equilibrium with the atmosphere. According to Henry's law the concentration, m, of a gas in a liquid is related to the partial pressure, p, of the gas and to the character of the gas and the liquid: $m = c_s p$. The numerical value of c_s, the coefficient of saturation (absorption), depends upon the units for expressing the concentration of the gas in the solution and its pressure, and upon the chemical character of the gas and the temperature and salinity of the water.

Table 40

COMPOSITION OF NORMAL ATMOSPHERE

Gas	Percent of volume or pressure	Partial pressure, Torr
Nitrogen	78.03	593.02
Oxygen	20.99	159.52
Argon	0.94	7.144
Carbon dioxide	0.03	0.228
Hydrogen, neon, helium	0.01	0.088
	100.00	760.000

With the exception of water vapor the relative composition of the atmosphere can be considered for practical purposes as constant (table 40). This does not strictly apply to carbon dioxide, relatively slight changes in the partial pressure of which have a pronounced effect upon the amount in solution, and hence upon the hydrogen ion concentration and other properties (p. 202). Because of the variability in the water vapor pressure, the saturation is always assumed to take place from a dry atmosphere at standard pressure, namely, 760 Torr. The natural fluctuations and regional differences in the atmospheric pressure are neglected.

The solubilities of those gases, such as oxygen and nitrogen, which do not react chemically with the water or its dissolved salts decrease with increasing temperature and salinity. The solubilities of oxygen and nitrogen in sea water of different salinities over the normal range of temperature were investigated by Fox (1907, 1909). Fox's values for oxygen are still the accepted standards, but his data for nitrogen have been superseded by those of Rakestraw and Emmel (1938b). The solubility of carbon dioxide is greater than that of oxygen and nitrogen because it reacts with the water. Part of the carbon dioxide is present as free CO_2 and H_2CO_3, but in sea water by far the greater part is present as carbonates and bicarbonate, and for the same partial pressure the total CO_2 content of sea water is much greater than that of distilled water or neutral salt solutions. The content of free CO_2 and H_2CO_3 decreases with increasing temperature and salinity. Argon is sometimes included with the "atmospheric nitrogen," and, because its solubility differs from that of nitrogen, the values of the saturation coefficients will be slightly modified. Little is known concerning the other gases in sea water; however, both hydrogen sulphide and ammonia are very soluble gases and their saturation values can play no important part in their distribution.

In table 41 are given values of the saturation coefficients (absorption coefficients) for oxygen, nitrogen, and carbon dioxide in fresh and sea water at different temperatures. The values for oxygen are from Fox (1909), as are also the values for nitrogen in distilled water. The other nitrogen values are from Rakestraw and Emmel (1938b). The values for carbon dioxide (Buch *et al*, 1932) correspond to the total CO_2 in water of zero alkalinity or to the free CO_2 and H_2CO_3 in sea water. It is seen that carbon dioxide is much more soluble than the other two gases and that oxygen is about twice as soluble as nitrogen.

From table 41 it is seen that within the range of chlorinity normally encountered in the oceans the temperature is the most important property influencing the solubility (see also tables 38, 39).

In studies of the distribution of dissolved gases in the sea it is generally assumed that, whatever the location of a water particle, at some time it has been at the surface and in equilibrium with the air. In their studies of the dissolved nitrogen content Rakestraw and Emmel (1938a) have found that the water is virtually saturated (referred to a normal atmosphere), regardless of depth; therefore this assumption appears

TABLE 41

COEFFICIENTS OF SATURATION OF ATMOSPHERIC GASES (c_s) IN WATER

(Concentrations of oxygen,[a] nitrogen,[b] and carbon dioxide[c] as ml/L and mg-atoms/L in equilibrium with 760 Torr = 1 atmosphere of designated gas)

Temperature	0°						12°						24°					
	O_2		N_2		CO_2		O_2		N_2		CO_2		O_2		N_2		CO_2	
Chlorinity (⁰/₀₀)	ml/L	mg-atoms O/L	ml/L	mg-atoms N/L	ml/L	mg-atoms C/L	ml/L	mg-atoms O/L	ml/L	mg-atoms N/L	ml/L	mg-atoms C/L	ml/L	mg-atoms O/L	ml/L	mg-atoms N/L	ml/L	mg-atoms C/L
0	49.24	4.40	23.00	2.06	1715	77.0	36.75	3.28	17.80	1.59	1118	50.2	29.38	2.62	14.63	1.31	782	35.1
16	40.1	3.60	15.02	1.73	1489	66.8	30.6	2.75	11.56	1.33	980	44.0	24.8	2.22	9.36	1.08	695	31.2
20	38.0	3.40	14.21	1.64	1438	64.5	29.1	2.61	10.99	1.26	947	42.5	23.6	2.12	8.96	1.03	677	30.4

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[a] Fox (1909).

[b] Distilled water, Fox (1909); sea water, Rakestraw and Emmel (1938b).

[c] Buch *et al* (1932), after Bohr. Concentrations represent amounts of free CO_2 and H_2CO_3.

valid and also indicates that biological activity involving either fixation or production of nitrogen cannot be sufficient to affect significantly the concentration of this gas in the water. As the waters of the oceans appear to have been saturated with oxygen and carbon dioxide at some stage in their history when they were at the surface, the differences between the saturation values (computed from the temperatures and salinities) and the observed contents are measures of the changes which have been effected by biological agencies. The factors influencing the distribution of carbon dioxide are discussed in the following sections, and the distribution of dissolved oxygen will be considered in many places in the ensuing chapters.

The Carbon Dioxide System

Although an extensive literature exists concerning the carbon dioxide system in sea water, publications prior to about 1929 are now chiefly of historic interest. The solution of the problems involved awaited not only the development of suitable analytical methods for the determination of the total carbon dioxide and the various forms in which it is present in sea water, but also the development of the theory and methods for studying the hydrogen ion concentration and certain general theories in physical chemistry. In the brief discussion to follow, only the salient features of the contemporary theories will be presented. These may be adequate for many purposes, but the investigations are not yet closed. Methods of analysis require further refinements, and in many cases fundamental constants must be more accurately determined.

Early investigators studying the carbon dioxide in sea water attempted to apply methods similar to those used for fresh water, where the carbon dioxide is largely present as free carbon dioxide that can be driven off by boiling, by applying a vacuum, or by bubbling through the water a stream of CO_2-free gas. The use of such methods on sea water gave variable and conflicting results. It was later found that in order to drive off all the CO_2 a strong acid must be added to the water, indicating that at least part of the carbon dioxide was present as the carbonate or bicarbonate of some basic cation. Methods were then developed for the determination of the total carbon dioxide and also for measuring the quantity present as carbonate and bicarbonate ions. It is now considered that the CO_2 can exist in the following forms in sea water and that under any given set of conditions equilibria will prevail:

$$CO_2(\text{dissolved}) \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^-(\text{bicarbonate}) \rightleftharpoons CO_3^=(\text{carbonate}).$$

If the gases in sea water are driven off by some suitable method, the CO_2 present as dissolved gas will be removed and the equilibria will be displaced until virtually all of the free CO_2 and carbonic acid are removed and the bicarbonate is all converted to carbonate. If a strong acid is added to sea water, the equilibria will be displaced toward the free CO_2; consequently, if sufficient acid is added, all the CO_2 is set free and can be determined either chemically or gasometrically. If an alkaline substance, such as sodium hydroxide, is added to sea water, the equilibria are shifted toward the carbonate, and the amount of carbonate ion will be increased. Although only a small fraction of the free CO_2 is hydrated to form H_2CO_3, in the following discussion the free $CO_2 + H_2CO_3$ will be referred to as carbonic acid and written H_2CO_3.

From the foregoing discussion it can be seen that the total CO_2 in sea water does not follow Henry's law for the solution of gases in *inert* solutions. Nevertheless, the partial pressure of the carbon dioxide in sea water in contact with the atmosphere will tend to establish equilibrium with that in the air. If the pressure is increased the amount in solution will be greater, and if it is reduced the quantity of CO_2 will decrease. The quantity present in a sample of water in equilibrium with a given carbon dioxide pressure will depend on the concentration of carbon dioxide bound base and the temperature and salinity of the water sample. If these factors are kept constant, the partial pressure of CO_2 can be used as a measure of the total carbon dioxide content of the water.

HYDROGEN ION CONCENTRATION (*p*H) OF SEA WATER. Sea water is normally alkaline. Since both the H^+ and OH^- ions play parts in the equilibria, any understanding of the carbon dioxide system requires knowledge of their concentrations. Pure distilled water dissociates into hydrogen and hydroxyl ions:

$$H_2O \rightleftharpoons H^+ + OH^-.$$

The ionic product $[H^+] \times [OH^-]$, when the concentrations are expressed in chemical equivalents per liter, varies somewhat with temperature, but at 25°C is 10^{-14} (p. 198). In pure water or in any solution that contains equal concentrations of H^+ and OH^- ions, the solution is said to be *neutral*. If the concentration of H^+ is in excess of OH^-, the solution is *acid*, and if less it is *alkaline*. The ionic product is a known function of the temperature and salt concentrations; hence, if $[H^+]$ or $[OH^-]$ is known, the other can readily be calculated. For expressing the hydrogen ion concentration, a logarithmic scale is commonly used, where *p*H is the logarithm of the reciprocal of the hydrogen ion concentration expressed as normality; that is, as equivalents per liter, $pH = \log \frac{1}{[H^+]}$. Thus, a neutral solution has a *p*H of approximately 7, an acid solution a *p*H less than 7, and an alkaline solution a *p*H greater than 7. It should be noted that a unit change in *p*H corresponds to a tenfold change in the hydrogen ion and hydroxyl ion concentrations.

The hydrogen ion concentration, or *p*H, of a solution may be determined in various ways, but all are essentially either electrometric or colorimetric. The hydrogen electrode, which is the standard for measuring hydrogen ion concentration, cannot be used for sea water, as it involves bubbling gas through the solution and, thus, disturbance of the carbon dioxide equilibrium. Two other electrometric methods are available—the quinhydrone electrode and the glass electrode. The quinhydrone method is not accurate in the *p*H range normally encountered, and the glass electrode has not yet been extensively applied to the study of sea water (Ball and Stock, 1937, Buch and Nynäs, 1939). Hence, virtually all of our knowledge concerning the hydrogen ion concentration in sea water is based on colorimetric methods.

Certain organic compounds classed as indicators have the property of changing color over a given range of hydrogen ion concentration. So-called bicolor indicators have one color when in an "acid" solution and another color when in an "alkaline" solution. For any indicator the color change takes place over a definite range in *p*H, and, at the hydrogen ion concentration that is numerically equal to the dissociation constant of the indicator, equal quantities of both color phases are present in the solution. The range in *p*H for which various indicators can be used is described by Clark (1928), who also gives in detail the methods for preparing the indicators. For sea water, cresol red and phenol red are generally used, as they cover the *p*H range normally found in the sea. When working in high *p*H ranges, bromthymol blue is commonly used.

Three important properties of *p*H indicators must be known before they can be applied to sea water: the dissociation constant of the indicator, the effect of temperature upon this value, and the salt error. The presence of neutral ions in the solution has a pronounced effect upon the color and, hence, upon the apparent *p*H as determined by indicators. This is known as the *salt error.* In general, neutral salts increase the apparent dissociation constant of the indicator, and therefore give low *p*H readings. In practice a carefully controlled quantity of an indicator solution is added to a sample of sea water, and either the color developed is compared to a set of tubes containing the equivalent quantity of indicator in solutions of known *p*H or the sample is examined in a bicolorimeter. The accepted colorimetric technique used for determining the *p*H of sea-water samples and the correction to be applied for salt error and temperature effects are described by Buch (1937) and by Buch and Nynäs (1939). Because of the effects of changes in temperature and pressure upon the dissociation constants of carbonic acid (p. 200) the measured *p*H of a sea-water sample will differ from the *p*H in situ. The magnitude of the temperature correction is given by Buch (1937), and the effect of pressure upon the *p*H has been studied by Buch and Gripenberg (see Buch *et al*, 1932).

The *p*H encountered in the sea is between about 7.5 and 8.4. That is, the hydrogen ion concentration ranges from 32×10^{-9} to 4×10^{-9}

equivalents per liter. The higher pH values are generally encountered at or near the surface. Where the water is in equilibrium with the CO_2 in the atmosphere, the pH is between about 8.1 and 8.3, but higher values may occur when the photosynthetic activity of plants has reduced the content of CO_2. Below the euphotic zone the pH shows a certain relationship to the amount of dissolved oxygen in the water. In regions where virtually all the oxygen has been consumed, and consequently where the total CO_2 is high, as at depths of about 800 m in the eastern portions of the Equatorial and North Pacific, the pH approaches a minimum value of 7.5. This is a limiting value, because no more CO_2 can be formed. Below the minimum oxygen layer there is generally a gradual increase in pH with depth. Under the peculiar conditions that may prevail in tide pools, bays, and estuaries, the pH sometimes exceeds the values cited above. Furthermore, in diluted water and in isolated basins where H_2S is produced the pH may approach 7.0 or even fall in the acid range.

ALKALINITY AND CARBON DIOXIDE COMPONENTS. The total amount of carbon dioxide in sea water, present either as free gas or bound, may be determined gasometrically after a strong acid has been added to the water to break up the carbonate compounds. Such a method has been described by Greenberg, Moberg, and Allen (1932). In order to determine the carbon dioxide components—namely, the amounts present as carbonic acid (including the free CO_2), bicarbonate, and carbonate—titrations must be made. For a given sample of sea water the amount of a strong acid (usually HCl about 0.01 normal) necessary to reduce the pH to about 4.5 is independent of the total CO_2. This amount of acid is required to set free the weak acids whose anions have been bound against basic cations. It is therefore not only a measure of the quantity of anions of weak acids in the sample, but also of the cations balanced against them. This quantity, when expressed as the number of milliequivalents of hydrogen ions (mg-atoms of H^+) necessary to set free the ions of weak acids in a volume of water which at 20° has a volume of 1 L, is known as the *alkalinity*. This quantity has also been referred to as the *titratable base*, *excess base*, *titration alkalinity*, and *buffer capacity*. The term *alkalinity* has been adopted as the standard designation by the International Association of Physical Oceanography (1939). It should be noted that the term as here defined has no relation to the hydroxyl ion concentration or to the fact that sea water is normally alkaline.

A number of methods have been suggested for determining the alkalinity, and these have been summarized by Thompson and Robinson (1932) and Gripenberg (1937b). In general, they follow one of two techniques. Either the titration is carried out in the presence of the carbon dioxide, in which case the end point is taken at about 4.5, or the carbon dioxide is driven off. In the latter case a higher pH, about

7.0, is used. When the carbon dioxide is driven off, an excess of acid may be added, the solution boiled to free it of CO_2, and then the excess acid determined by titration; or the measurement may be made directly upon the sample, which is held at the boiling point during the titration. Another method has been to add a known quantity of acid to the sample of sea water and then to determine the *p*H (Mitchell and Rakestraw, 1933). It has been implied that all of these methods will give the same value for the alkalinity, but this is not necessarily the case, and it is hoped that a standard method will be established.

The alkalinity bears a fairly constant relation to the chlorinity. The alkalinity:chlorosity factor for surface water has been determined by a number of workers and found to be close to 0.120 when the alkalinity is expressed in terms of milligram-atoms. The designation *specific alkalinity* that has been used in some cases is obtained by dividing the alkalinity, as mg-atoms/L, by the chlorinity, in g/kg, but such a mixed ratio should not be used. In water from greater depths the ratio may be somewhat higher than that given above, approaching an upper limit of 0.125 near the sea floor (Wattenberg, 1933). In brackish water the ratio may be increased tremendously if the river water is high in bound carbonate compounds. When the alkalinity:chlorosity factor is to be used as an index in studies of industrial pollution, the "normal" change in the ratio with concentration must first be established in samples of sea water diluted with unpolluted river water. Observations by Moberg and Revelle (1937) and by Wattenberg (1936) have shown that in oceanic water the increase in the Ca:*Cl* factor with depth is equivalent to the rise in the alkalinity:*Cl* factor. This indicates that changes in the alkalinity and calcium are of common origin—namely, precipitation or solution of $CaCO_3$. Further material concerning the regional variations in the alkalinity:chlorosity factor is given on p. 208.

Because variations in the alkalinity:chlorosity factor in oceanic water are associated with corresponding changes in the calcium:chlorosity factor, the calcium content of the water may be computed from the alkalinity by the following expression:

$$\text{Ca(mg-atoms/L)} = \frac{\text{alkalinity}}{2} + 0.465 \times \text{chlorosity}.$$

This procedure for estimating calcium has been followed by Wattenberg (for example, Wattenberg, 1936).

It may be seen that the alkalinity:chlorosity factor of 0.1205 is the same as the $HCO_3^-:Cl$ factor given in table 35, when the bicarbonate is expressed as milligram-atoms of carbon per liter. The reason for this identity is that, in preparing the table, it was assumed that the *p*H of the water was such that only bicarbonate ions were present and, hence, would be equivalent to the alkalinity.

In discussions of the carbon dioxide system in sea water, the concentrations of the components have commonly been given in millimoles per liter. These are numerically identical with concentrations given as mg-atoms/L of carbon.

Salts of weak acids containing the following elements are known to occur in sea water: carbon, boron, phosphorus, arsenic, and silicon. Of these, salts of carbonic and boric acid only are present in sufficient concentrations to affect the magnitude of the alkalinity. For the present, we shall neglect the boric acid, which does not affect the alkalinity determination and which has to be considered in the carbonate system only at higher *p*H's. The alkalinity may then be taken as a measure of the concentration of bicarbonate and carbonate ions, and

$$[A] = [HCO_3^-] + 2[CO_3^=],$$

where the brackets indicate *molar* concentrations—that is, *gram-atoms* of carbon per liter. The $[H_2CO_3]$ may be determined by titration with sodium hydroxide and the $[CO_3^=]$ by titration with acid, using carefully controlled end points. The method is described by Greenberg, Moberg, and Allen (1932). It is shown later that the concentration of either H_2CO_3 or $CO_3^=$ will be negligible when the other is present in significant quantities. Therefore we may write:

$$[\Sigma CO_2] = [H_2CO_3] + [HCO_3^-] \qquad \text{and} \qquad [A] = [HCO_3^-],$$

or

$$[\Sigma CO_2] = [HCO_3^-] + [CO_3^=] \qquad \text{and} \qquad [A] = [HCO_3^-] + 2[CO_3^=].$$

By substituting in these equations the measured quantities, the other components may be obtained.

Studies of the carbon dioxide system based on measurements made by these methods have been reported by Greenberg, Moberg, and Allen (1932) and Moberg, Greenberg, Revelle, and Allen (1934). In fig. 38 are shown vertical distribution curves for the carbon dioxide components, total carbon dioxide calculated from the titrations and by direct gasometric measurements, and the alkalinity at a station off the coast of southern California. The total CO_2 obtained by the two methods agrees very well and shows a general increase with depth. In the upper layers there is an appreciable amount of $CO_3^=$, but this decreases to zero at 200 m, and below this level H_2CO_3 occurs in quantities which increase with depth. The alkalinity is indicated for the upper 200 m, below which it corresponds, of course, to the curve showing the amount of HCO_3^-. The increase of alkalinity with depth may be partly due to the biological precipitation of $CaCO_3$ in the upper layers, but in this area it is principally associated with the increasing salinity.

We shall now proceed to a discussion of the laws governing the equilibria between the various carbon dioxide components, the alkalinity, and the partial pressure of CO_2. Thus far it has been assumed that the alkalinity was a measure of the equivalents of HCO_3^- and $CO_3^=$ ions and of the cations bound against them, but this concept must be modified somewhat. Hydrogen and hydroxyl ions must also be taken into account, and, at the higher pH's, the boric acid as well. Since boric acid is a weak acid, only the first dissociation stage need be considered. The balance between the ions with which we are concerned may be written

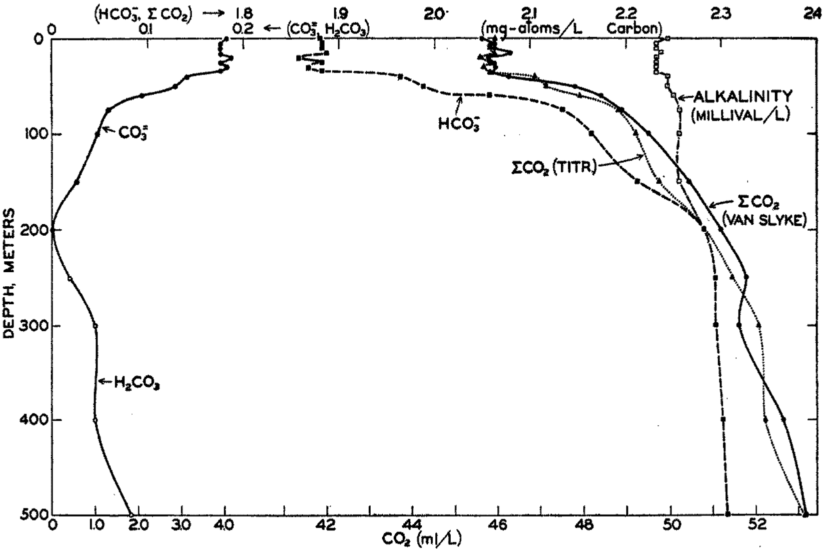

Fig. 38. Vertical distribution of the alkalinity and carbon dioxide components off southern California.

$$[A] + [H^+] = [HCO_3^-] + 2[CO_3^=] + [H_2BO_3^-] + [OH^-].$$

If we indicate the portion of the base (alkalinity) directly bound to the carbon dioxide components as A_{CO_2}, the relationship may be written (Buch, 1933a,b)

$$[A_{CO_2}] = [A] - \frac{K'_B \times [\Sigma H_3BO_3]}{[H^+] + K'_B} + [H^+] - \frac{K_W}{[H^+]},$$

where all concentrations are in gram-atoms per liter. K'_B is the apparent first dissociation constant of boric acid in sea water at the particular temperature and salinity prevailing, and K_W is the ionic concentration product of water, $[H^+] \times [OH^-]$, under similar conditions. According to Buch (1938) the ionic product in sea water at 20° can be computed from the following equation:

$$pK_W = 14.170 - 0.1517\sqrt[3]{Cl} + 0.0083\ Cl.$$

pK_W decreases by about 0.035 for each 1-degree rise in temperature

(Dorsey, 1940). The expression pK_W bears the same relation to K_W that pH does to $[H^+]$ and is the logarithm of the reciprocal of the ionic product. The same convention is used in expressing dissociation constants. The total concentration of boric acid $[\Sigma H_3BO_3]$ can be obtained from the chlorosity:

$$[\Sigma H_3BO_3] = 0.0221 \times \text{chlorosity} \times 10^{-3}.$$

According to Buch the dissociation constant of boric acid can be expressed as

$$pK'_B = 9.22 - 0.123\sqrt[3]{\text{Cl}} - 0.0086\ \text{Cl}.$$

The correction to be applied to the alkalinity to obtain A_{CO_2} is appreciable at the higher pH's, as can be seen from fig. 39, where the quantities are given as milliequivalents per liter.

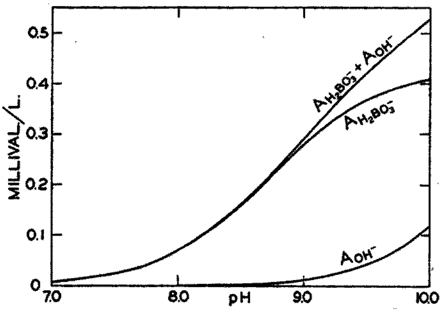

Fig. 39. Concentrations of hydroxide-bound (A_{OH^-}) and borate-bound ($A_{H_2BO_3^-}$) base as a function of pH in water of Cl = 19.00 $^0/_{00}$ at 20°C.

The equation for the first dissociation constant of carbonic acid is

$$\frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} = K'_1,$$

and for the second:

$$\frac{[H^+] \times [CO_3^=]}{[HCO_3^-]} = K'_2,$$

where the brackets indicate molar concentrations. By introducing the relationships

$$[A_{CO_2}] = [HCO_3^-] + 2[CO_3^=]$$

and

$$[\Sigma CO_2] = [H_2CO_3] + [HCO_3^-] + [CO_3^=],$$

it is possible to eliminate HCO_3^- and $CO_3^=$ from the above equations and obtain them in the following form:

$$\frac{[H^+] \times [A_{CO_2}]}{\left(1 + \frac{2K'_2}{[H^+]}\right) \times [\Sigma CO_2] - \left(1 + \frac{K'_2}{[H^+]}\right) \times [A_{CO_2}]} = K'_1$$

$$\frac{[H^+] \times \left\{\left(1 + \frac{[H^+]}{K'_1}\right) \times [A_{CO_2}] - [\Sigma CO_2]\right\}}{2[\Sigma CO_2] - [A_{CO_2}]} = K'_2.$$

Extensive investigations have been carried out to determine the magnitudes of K'_1 and K'_2. These studies have been reported by Buch, Harvey, Wattenberg, and Gripenberg (1932), and by Moberg, Greenberg, Revelle, and Allen (1934). Buch and others have followed up the work, using more refined methods and theories. According to Buch *et al* (1932),

$$pK_1' = 6.47 - 0.188\sqrt[3]{\mathrm{Cl}} \text{ at } 20°\mathrm{C}.$$

Corrections for temperature can be computed from the following expressions:

Near 20°C, $\Delta pK_1' = -0.006\Delta\vartheta$.
Near 5°C, $\Delta pK_1' = -0.009\Delta\vartheta$.

The effect of hydrostatic pressure, as expressed by means of the depth Δz in meters, on the first dissociation constant is

$$\Delta pK_1' = -0.48 \times 10^{-4}\Delta z.$$

Buch (1938) found that the second dissociation constant of carbonic acid in sea water at 20°C may be computed from the following equation:

$$pK_2' = 10.288 - 0.443\sqrt[3]{\mathrm{Cl}} - 0.0046\,\mathrm{Cl}.$$

Over the normal range of chlorinity in sea water a simpler expression is adequate—namely,

$$pK_2' = 10.35 - 0.498\sqrt[3]{\mathrm{Cl}}.$$

The temperature and pressure corrections are

$$\Delta pK_2' = -0.011\Delta\vartheta(\text{at } 20°).$$
$$\Delta pK_2' = -0.012\Delta\vartheta(\text{at } 5°).$$
$$\Delta pK_2' = -0.18 \times 10^{-4}\Delta z.$$

For any given set of conditions, as expressed by means of temperature, salinity, pressure, alkalinity, and *p*H, the values of A_{CO_2} and K_1' and K_2' can be calculated. From these the total carbon dioxide and its various components can be computed from the following equations (Revelle, 1934):

$$[\Sigma\mathrm{CO}_2] = \frac{[A_{\mathrm{CO}_2}]}{1 + \dfrac{2K_2'}{[\mathrm{H}^+]}} \times \left(\frac{[\mathrm{H}^+]}{K_1'} + \frac{K_2'}{[\mathrm{H}^+]} + 1\right).$$

$$[\mathrm{HCO}_3^-] = \frac{[A_{\mathrm{CO}_2}]}{1 + \dfrac{2K_2'}{[\mathrm{H}^+]}}$$

$$[\mathrm{CO}_3^=] = \frac{[A_{\mathrm{CO}_2}]}{1 + \dfrac{2K_2'}{[\mathrm{H}^+]}} \times \frac{K_2'}{[\mathrm{H}^+]}.$$

$$[\mathrm{H}_2\mathrm{CO}_3] = \frac{[A_{\mathrm{CO}_2}]}{1 + \dfrac{2K_2'}{[\mathrm{H}^+]}} \times \frac{[\mathrm{H}^+]}{K_1'}.$$

In fig. 40 are shown the variations in the carbon dioxide components with *p*H, calculated from the equations given above for sea water of

$\mathrm{Cl} = 19\ ^0/_{00}$ at $\vartheta = 20°\mathrm{C}$, and at atmospheric pressure. The CO_2 components are given as mg-atoms/L of carbon and as ml/L of CO_2.

The partial pressure of carbon dioxide is related to the amount of free $CO_2 + H_2CO_3$ (indicated as H_2CO_3; see p. 190) in the solution:

$$p_{CO_2} = \frac{[H_2CO_3]}{c_s \times 10^{-3}}.$$

The value of c_s (p. 191) depends upon the temperature and salinity and the units used for expressing the concentration and partial pressure.

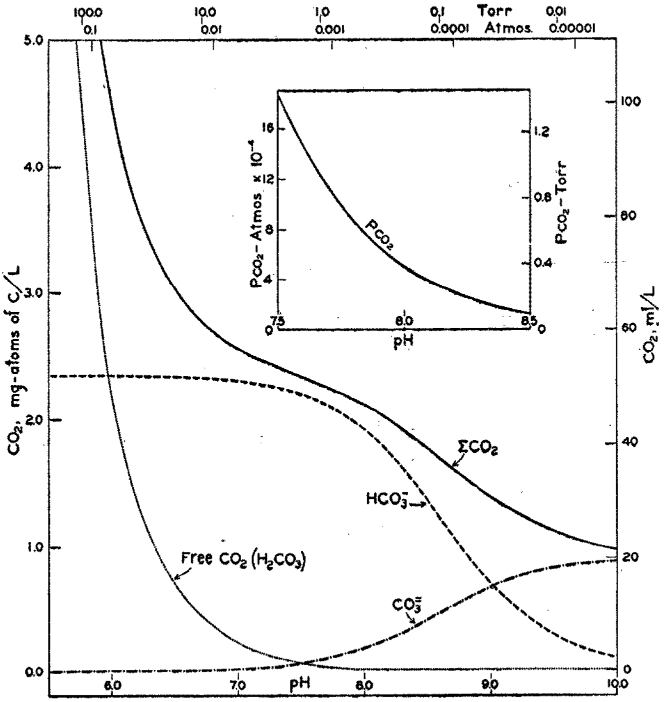

Fig. 40. Carbon dioxide components in sea water of $\mathrm{Cl} = 19.00\ ^0/_{00}$ at 20°C as a function of pH and the partial pressure of carbon dioxide.

In fig. 41 are shown curves for c_s at different temperatures and chlorinities, where they represent the amount of H_2CO_3, in milligram atoms of carbon per liter of sea water, in solution under the designated conditions when the partial pressure of CO_2 is 1 physical atmosphere (760 Torr). At 20° and $19\ ^0/_{00}$ Cl, c_s is 34.2. That is, a partial pressure of one atmosphere of CO_2 would be in equilibrium with a solution containing 34.2 milligram-atoms of carbon as free $CO_2 + H_2CO_3$. The data are from Buch *et al* (1932).

The variations in p_{CO_2} with the other components is shown in fig. 40. The range is from less than 0.01 to greater than 100 Torr (0.1×10^{-4} to 1000×10^{-4} atm). The relationship over the pH range normally encountered in sea water is shown in the inset diagram in fig. 40. Between pH 7.5 and 8.3, p_{CO_2} decreases from 1.4 to 0.15 Torr (18.0 to 2.0×10^{-4} atm). The average partial pressure of CO_2 in the air is about 0.23 Torr; hence surface sea water of Cl = 19.0 $^0/_{00}$ at 20° will have a pH of 8.2 if it is in equilibrium with the atmosphere.

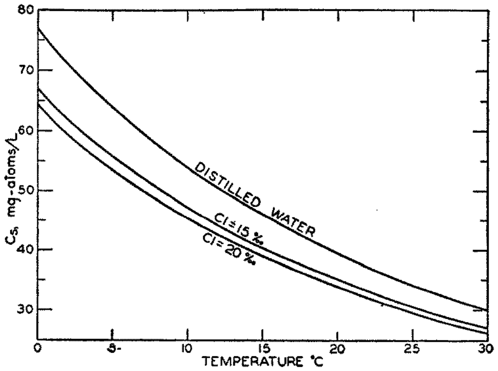

Fig. 41. Absorption coefficient (c_s) of carbon dioxide in sea water as a function of temperature and chlorinity.

Sea water is a very favorable medium for the development of photosynthetic organisms. It not only contains an abundant supply of CO_2, but removal or addition of considerable amounts results in no marked changes of the partial pressure of CO_2 and the pH of the solution, both of which are properties of importance in the biological environment (p. 268). If the CO_2 available for photosynthesis is assumed to be $H_2CO_3 + \frac{1}{2}HCO_3^-$, 0.48 mg-atoms of carbon per liter may be removed from water of Cl = 19 $^0/_{00}$ with an increase of the pH from 7.5 to only 8.5. In distilled water or in an inert salt solution of zero akalinity initially at pH 7.5, the total CO_2 would be about one seventh of that amount.

Buffer Action of Sea Water. If a small quantity of a strong acid or base is added to pure water, there are tremendous changes in the numbers of H^+ and OH^- ions present, but the changes are small if the acid or base is added to a solution containing a weak acid and its salts or a weak base and its salts. This repression of the change in pH is known as *buffer action*, and such solutions are called *buffer solutions*. Sea water contains carbonic and boric acids and their salts and is, therefore, a buffer solution. Let us consider only the carbonate system. Carbonate and bicarbonate salts of strong bases, such as occur in sea water, tend to hydrolyze, and there are always both H^+ and OH^- ions in the solution. If an acid is added, carbonate is converted to bicarbonate and the bicarbonate to carbonic acid, but, as the latter is a weak acid (only slightly dissociated), relatively few additional hydrogen ions are set free. Similarly, if a strong base is added, the amount of carbonate increases, but the OH^- ions formed in the hydrolysis of the carbonate increase only slightly. The buffering effect is greatest when the hydrogen ion concentration is equal to the dissociation constant of the weak acid or base—that is, when the concentration of the acid is equal to that of its salt.

Cycle of CO_2 between Sea and Atmosphere. Investigations of the partial pressure of CO_2 in the ocean and the atmosphere have been made by Krogh (1904) and Buch (1939a,b). The following internal changes will increase or decrease the p_{CO_2} in the surface layer:

Increase p_{CO_2}	*Decrease* p_{CO_2}
1. Rise in temperature	1. Decrease in temperature
2. Rise in salinity (evaporation)	2. Decrease in salinity
3. Respiration	3. Photosynthesis
4. Precipitation of $CaCO_3$	4. Solution of $CaCO_3$
5. Deep water brought to surface	

The partial pressure of CO_2 in the surface water can be computed with sufficient accuracy when the temperature, salinity, alkalinity, and *p*H are known, but, before a better understanding of the CO_2 exchange between the sea and the atmosphere can be obtained, a far more comprehensive study of the partial pressure of the atmospheric CO_2 must be made. Buch (1939b) has reported a number of direct observations on the CO_2 content of the air which indicate that polar air is relatively low in CO_2 ($p_{CO_2} = 0.23$ Torr), compared to continental and tropical air ($p_{CO_2} = 0.25$ Torr). It has been suggested that in low latitudes the air is enriched with CO_2 from the ocean and that the general atmospheric circulation carries the CO_2 into high latitudes. There it again dissolves in the sea water, which in time brings it back toward the Equator.

Activity of Ions in Sea Water. The apparent first and second dissociation constants of carbonic acid and the first dissociation constant of boric acid in sea water are larger than in distilled water and increase with increasing salinity. That is, the strength of these acids appears to be greater in solutions containing salts. These phenomena can be accounted for on the theory of activity introduced by Lewis and Randall (1923) and developed mathematically by Debye and Hückel. In a solution containing a mixture of electrolytes, such as sea water, there is a mutual interference of the ions, so that their activity or ability to participate independently in some reaction is much reduced. Most chemical determinations measure the total concentration of some ion and not its activity; however, certain physical measurements show the activity. For example, electromotive force determinations involve the activity of the hydrogen and other ions. Similarly, the measurement of the vapor pressure of a solution of a nonvolatile compound is an indication of the activity of the solvent. The activity will be less than that of the pure solvent under similar conditions. The partial pressure of dissolved gases is a measure of their activity.

The activity coefficient γ is related to the activity α of an ion as in the following example:

$$\gamma_{\mathrm{H}^+} \times [\mathrm{H}^+] = \alpha_{\mathrm{H}^+}.$$

Hence, α_{H^+} is the activity of the hydrogen ions expressed as gram-atoms per liter and $[\mathrm{H}^+]$ is the stoichiometric concentration.

In the studies of the carbon dioxide system in sea water, the total CO_2, alkalinity, and carbon dioxide components are measured chemically, and hence the values represent the stoichiometric values and not the activities. On the other hand, the hydrogen ion concentration is determined colorimetrically or electrometrically, and these methods yield the activity of hydrogen ions directly. Therefore, in the equations relating the CO_2 components α_{H^+} could have been inserted instead of $[\mathrm{H}^+]$. The dissociation constants have been referred to as *apparent* dissociation constants, in contrast to the *thermodynamic* constants that would be obtained at infinite dilution, where the activity coefficients (γ) are unity. The apparent dissociation constants are indicated by the symbol prime ($'$)—for example, K_2'. For carbonic acid the thermodynamic second dissociation constant can be written

$$K_2 = \frac{\alpha_{\mathrm{H}^+} \times \gamma_{\mathrm{CO}_3^=} \times [\mathrm{CO}_3^=]}{\gamma_{\mathrm{HCO}_3^-} \times [\mathrm{HCO}_3^-]},$$

and this is related to the apparent dissociation constant (Moberg *et al*, 1934):

$$pK_2 = pK_2' + \log \frac{\gamma_{\mathrm{HCO}_3^-}}{\gamma_{\mathrm{CO}_3^=}}.$$

Similarly,

$$pK_1 = pK_1' + \log \frac{\gamma_{\mathrm{H_2CO_3}}}{\gamma_{\mathrm{HCO}_3^-}}.$$

The value of $\gamma_{\mathrm{H_2CO_3}}$ depends upon the relative solubility of CO_2 in pure water and in sea water at the same temperature and upon the activity of the water in the two cases:

$$\gamma_{\mathrm{H_2CO_3}} = \frac{c_o}{c_s} \times \frac{e_s}{e_o}.$$

The subscript *o* indicates values at infinite dilution, and the subscript *s* the values at the concentration under consideration. The values of c_o and c_s can be obtained from fig. 41, and e_s and e_o (the vapor pressures) can be computed (p. 67).

From the empirical equations relating pK_1' and pK_2' to the temperature and chlorinity, we know that at 20° and zero chlorinity the thermodynamic values are $pK_1 = 6.47$ and $pK_2 = 10.288$, and, at 19.00 $^0/_{00}$ Cl, $pK_1' = 5.97$ and $pK_2' = 9.02$. By substituting these values and $\gamma_{\mathrm{H_2CO_3}}$

(in this case 1.131), it is possible to determine the activity coefficients for the carbonate and bicarbonate ions. This substitution yields

$$\gamma_{HCO_3^-} = 0.36, \qquad \gamma_{CO_3^=} = 0.019.$$

Thus, in sea water of 19.00 ‰ Cl at 20°, only about one third of the bicarbonate and one fiftieth of the carbonate ions are "active." This will be considered again with reference to the solubility of $CaCO_3$.

Empirical equations have been presented which relate pK_1' and pK_2' to the cube root of the chlorinity. It has been shown (Buch *et al*, 1932, Moberg *et al*, 1934) that these equations are generally valid for salt solutions other than sea water if the ionic strength is used instead of chlorinity as a measure of concentration. The ionic strength (μ) of a solution is obtained by first multiplying the concentration of each individual type of ion, in moles per kilogram of solvent water, by the square of its valence, and then taking half the sum of these products (Lewis and Randall, 1923, p. 373). Lyman and Fleming (1940) have shown that the ionic strength of sea water in the normal range of concentration may be computed from the expression

$$\mu = 0.00147 + 0.03592\ \mathrm{Cl} + 0.000068\ \mathrm{Cl}^2.$$

Moberg *et al* (1934) have summarized the pertinent data, but no satisfactory expressions have yet been developed to show the manner in which the activity coefficients of the different ions in sea water change with concentration.

Solubility of $CaCO_3$. The solubility of an electrolyte, such as calcium carbonate, may be expressed by a *solubility product.* The solubility product is identical with the ionic product (if concentrations are expressed as moles per liter) when the solution is in equilibrium with the solid salt and, therefore, saturated. The value of the solubility product depends upon temperature, the concentration of other ions (salinity), and the hydrostatic pressure. If, under a given set of conditions, the ionic product is less than the solubility product, the solution is undersaturated; if the ionic product is greater the solution is supersaturated, and if suitable nuclei are present, precipitation will proceed until the ionic product equals the solubility product.

The solubility product of $CaCO_3(K_{CaCO_3})$ in distilled water at 20° is 5.0×10^{-9}. In sea water of chlorinity 19.00 ‰ and at the same temperature, the calcium content is 10.23 mg-atoms/L, and at pH 8.2 the carbonate ion concentration is 0.26 mg-atoms/L of carbon. Therefore the ionic product is

$$[Ca^{++}] \times [CO_3^=] = 10.23 \times 0.26 \times 10^{-6} = 2.66 \times 10^{-6},$$

which is 530 times greater than the solubility product in distilled water. If solubility data for distilled water are to be applied to sea water, it is necessary to take the activity of the ions into account. It has been shown (p. 205) that the activity of the $CO_3^=$ ions is about 0.02, and introducing this correction reduces the *apparent* supersaturation to about tenfold. Since no data are yet available for the activity of the Ca^{++} ions in sea water, it is impossible to apply solubility products determined for distilled water to test the relative saturation of calcium carbonate and other salts in sea water.

It is therefore necessary to determine empirically the concentrations of Ca^{++} and $CO_3^=$ that can exist in contact with solid $CaCO_3$. Working at 30° and increasing the $CO_3^=$ content by lowering the total CO_2, Revelle and Fleming (1934) obtained precipitation of $CaCO_3$ as aragonite needles and spherulites. The calcium content of the solution was determined directly, and the $CO_3^=$ was calculated from measurements of the *p*H, alkalinity, and chlorinity. The average of three experiments gave $K'_{CaCO_3} = 2.4 \times 10^{-6}$ at 30°C. Wattenberg has carried out a number of studies on the solubility of calcium carbonate in sea water. His general procedure was to add $CaCO_3$ crystals to sea water, and in some instances to increase the p_{CO_2}. The sea-water samples were then placed in sealed flasks and agitated until equilibrium was established. The calcium content of the water was calculated from the alkalinity measurements (p. 196), and the $CO_3^=$ was obtained with the aid of *p*H determinations. Wattenberg and Timmerman (1936) give the following values for the apparent solubility product in sea water of Cl = 18.5 to 19.5 ‰:

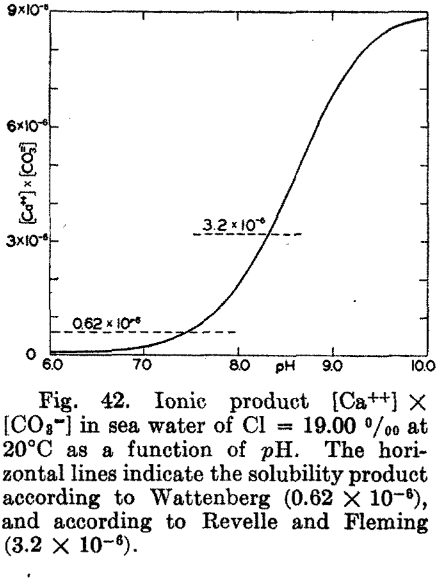

Fig. 42. Ionic product $[Ca^{++}] \times [CO_3^=]$ in sea water of Cl = 19.00 ‰ at 20°C as a function of *p*H. The horizontal lines indicate the solubility product according to Wattenberg (0.62×10^{-6}), and according to Revelle and Fleming (3.2×10^{-6}).

Temperature, °C	0	5	10	15	20	25	30	35
K'_{CaCO_3}	8.1	7.9	7.4	6.8	6.2	5.5	4.7	3.8×10^{-7}

At 30° Wattenberg's value is only one fifth of that obtained by Revelle and Fleming. No satisfactory explanation of this difference has yet been offered. In fig. 42 the ionic product in sea water of Cl = 19.00 ‰ at 20° is plotted against *p*H. The value of K'_{CaCO_3} for this temperature obtained by Wattenberg—namely, 0.62×10^{-6}—would indicate that supersaturation exists at all *p*H's above about 7.5. Surface water in equilibrium with the atmosphere has a *p*H of about 8.2 and would be about sixfold supersaturated. The K'_{CaCO_3} obtained by Revelle and Fleming, on the other hand, if corrected to 20°, would be 3.2×10^{-6}, which would indicate that surface water is about saturated with $CaCO_3$ under these conditions. It hardly seems likely that surface sea water can be as highly supersaturated as Wattenberg's values would indicate. As an explanation it has been suggested that the calcium carbonate may not be free as ions but may be present in some complex, or possibly as colloidal calcium carbonate. On the other hand, it may be that the empirically determined values of K'_{CaCO_3} are not applicable to sea water because of lack of equilibrium or faulty experimental technique. Further studies must be made before these points can be decided.

Smith (1940) has investigated the calcium carbonate deposition that takes place in the shallow waters overlying the Bahama Banks. He found the alkalinity to be much reduced, and from measurements he computed the ionic product, $[Ca^{++}] \times [CO_3^{=}]$. Minimum values of the product that he considers approach the solubility product were found to fall between the values of Revelle and Fleming and those of Wattenberg.

According to Wattenberg (1936), K'_{CaCO_3} at 20° changes with the chlorinity in the following way:

Cl, ‰	0	5	10	15	20
K'_{CaCO_3}	0.05	1.8	4.0	5.0	6.2×10^{-7}

That is, in sea water the apparent solubility product of $CaCO_3$ increases with chlorinity and decreases with temperature.

Revelle (1934) and Wattenberg (1936) consider that hydrostatic pressure has no significant effect upon the value of K'_{CaCO_3}. However, it should be remembered that, because of changes in the dissociation constants of carbonic acid, pressure does modify the relative amounts of HCO_3^- and $CO_3^=$ in the water. Hence, water that is saturated at the surface will be slightly undersaturated if subjected to hydrostatic pressure, even if the total CO_2 and calcium contents remain unaltered. Conversely, bottom water saturated with $CaCO_3$ will be supersaturated when brought to the surface.

Although our knowledge of the values of K'_{CaCO_3} under different conditions is incomplete and uncertain, it is possible to show the effect of changes in the conditions upon the ionic product, thus obtaining an understanding of those agencies that will favor precipitation or solution. Revelle (1934) has shown that, in surface water, increase of the salinity and the temperature, and decrease of the p_{CO_2}—that is, the total CO_2 content—all tend to increase the ionic product and therefore favor precipitation. The salinity effect is relatively small, and hence areas of high or rising temperature and of active photosynthesis will be those where precipitation of $CaCO_3$ is most likely to occur. Opposite conditions will favor solution.

In the deep water the range in temperature and salinity is small, and therefore the variations in p_{CO_2} will have the most pronounced effect. According to Wattenberg's studies (1933) the deep waters of the Atlantic Ocean are virtually saturated with calcium carbonate. Areas overlying red clay show slight undersaturation, and those overlying calcareous deposits (globigerina ooze) show either saturation or slight supersaturation.

Certain types of calcareous sedimentary material, both recent and fossil, do not show any evidence of organic origin. These are sometimes considered to be "chemical" deposits. In certain areas, microorganisms undoubtedly play an important part in establishing conditions that result in the incidental precipitation of carbonates. In tropical seas, this process may occur in shoal-water areas, coral reefs, lagoons, and mangrove swamps (Field, 1932). Although microorganisms can produce conditions favoring the precipitation of calcium carbonate, it is considered that they are effective agents in this process only in and on the sediments in the environments listed above. Smith (1940) has found that over the Great Bahama Bank $CaCO_3$ is precipitated, under conditions of heating and excessive evaporation, on nuclei supplied by the sediments. The finely divided $CaCO_3$ in certain deep-sea sediments is thought to arise from the break-down of the shells of foraminifera (p. 982) and not from precipitation *in situ.*

DISTRIBUTION OF ALKALINITY, *p*H, AND CARBON DIOXIDE COMPONENTS. In the preceding discussion it has been assumed that the alkalinity: chlorosity factor is constant, and the value 0.1205 (milliequivalents per unit *Cl*) has been used in computations. This is in agreement with the average of a large number of observations made by Wattenberg (1933) in the Atlantic Ocean and those reported by Revelle (1936) for the upper layers of the Pacific Ocean. Wattenberg's value is commonly given as the specific alkalinity—namely, as milliequivalents per unit chlorinity, in which case it is 0.123. A number of different methods (p. 195) have been employed for measuring alkalinity, but there is no definite proof that they all yield similar values. Hence, it is difficult to compare the results obtained from various parts of the oceans by different workers. However, the findings of Wattenberg (1933), Mitchell and Rakestraw (1933), and Revelle (1936) all show that there is a somewhat higher alkalinity:chlorosity factor in the deeper water than there is in the surface layers. The increase in the factor usually amounts to about 0.005. Wattenberg examined a number of water samples collected immediately over the bottom, and in these he found an even larger factor. The low values in the surface waters are ascribed to removal of calcium carbonate by organisms possessing calcareous skeletons. Smith (1940) has suggested that, at least in certain localities, there may be inorganic precipitation if suitable nuclei are present when the water is undergoing heating and evaporation. Whether or not calcium carbonate dissolves again while sinking through the water column depends upon the degree to which the water is saturated with this compound. The production of CO_2 by metabolic activity at subsurface levels will favor solution. This production also occurs in the sediments and probably accounts for the sharp increase in alkalinity immediately over the bottom, which was detected by Wattenberg. Revelle (1936) has offered evidence which indicates that the alkalinity:chlorosity factor is higher in the North Pacific Ocean than it is in the Atlantic. The greater alkalinity may be attributed to the lower dissolved oxygen content of the intermediate and deep waters of the North Pacific. The lower oxygen content is indicative of a higher content of carbon dioxide, and hence greater solubility of calcium carbonate. Wattenberg's data indicate that the variation in the alkalinity:chlorosity factor with depth is much less in high latitudes, where organisms with calcareous skeletons are less abundant or are lacking and where vertical mixing produces more uniform conditions. That the change in alkalinity is analogous to variations in calcium content of the water has been pointed out by Moberg and Revelle (1937). River water contains relatively large proportions of calcium carbonate, and in regions of marked dilution there are great increases in the alkalinity:chlorosity factor. It may also be modified by the formation and melting of sea ice (p. 216).

The *p*H of sea water in contact with the air will vary between about 8.1 and 8.3, depending upon the temperature and salinity of the water and the partial pressure of carbon dioxide in the atmosphere. In areas of great dilution lower values may occur. At subsurface levels, where exchange of carbon dioxide with the atmosphere is impossible, the *p*H will vary with the extent to which the CO_2 content of the water is modified by biological activity. In the euphotic zone, higher *p*H's are usually found; below this they decrease to a minimum corresponding in general to the layer of minimum oxygen content, and then increase again toward the bottom. Although variations in the salinity affect the *p*H, the predominant factor is the total carbon dioxide content or its partial pressure.

Unfortunately, differences in technique and in the constants used in arriving at *p*H's from colorimetric measurements make it difficult to compare the results of different workers. The most extensive studies made on the distribution of *p*H in the oceans are those of the *Meteor* (Wattenberg, 1933) in the Atlantic Ocean and those of the *Carnegie* in the Pacific Ocean. The distributions of *p*H and dissolved oxygen along a longitudinal profile in the eastern Atlantic Ocean are shown in fig. 43. The rather close similarity of the isolines can easily be seen, and similar patterns would be given by the partial pressure and total CO_2 content, although in this case the relations would be inverse ones. The temperature and salinity of the water are of secondary importance in determining the *p*H. In the North Pacific, where the oxygen content is low at intermediate and greater depths, when compared to the Atlantic, the *p*H is somewhat lower and approaches 7.5 where the oxygen content is reduced to less than a few tenths of a milliliter per liter. In stagnant basins (Ström, 1936) where large amounts of H_2S are present, the *p*H may approach 7.0. The total CO_2 content of water in contact with the air is chiefly dependent upon the alkalinity—that is, the salinity—and to some extent upon the temperature. Regional variations in the partial pressure of carbon dioxide in the atmosphere may cause some variations. Below the surface the total carbon dioxide content and, hence, the magnitude of the different components are primarily determined by the changes in the carbon dioxide content resulting from photosynthesis or respiration. If the temperature, salinity, and depth, and two of the following variables—*p*H, alkalinity, or p_{CO_2}—are known, all components may be computed from equations given on p. 200.

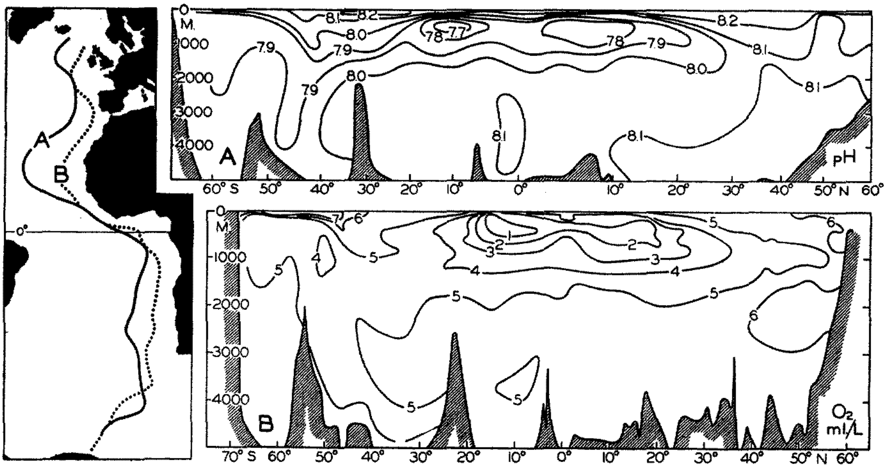

Fig. 43. Distribution of *p*H and dissolved oxygen in the eastern part of the Atlantic Ocean. The locations of the sections are shown in the map on the left-hand side. The vertical and horizontal scales are different in the two sections. (After Wattenberg.)

Solubility of Salts in Sea Water

The solubility of calcium carbonate in sea water has been examined in some detail, but relatively little is known about the other constituents. Because of the complex nature of sea water and the effect of other ions upon the activity of any one, the solubility product of a single salt in distilled water cannot be applied to sea water. Cooper (1937b) considers that most of the iron in sea water is not in true solution, but is present in some colloidal form, as the solubility product for the hydroxide is extremely small. Wattenberg and Timmermann (1938) studied the solubilities of magnesium and strontium carbonates and magnesium hydroxide in sea water. The data in table 42 are from their work. It is interesting to note the great increase in the apparent solubility products in sea water, which is due to the reduced activity of the participating ions. For comparison, the ionic products for sea water (19.00 $^0/_{00}$ Cl, $\vartheta = 20°$) at pH 8.2 have been computed. The apparent supersaturation of the calcium carbonate is discussed in the preceding pages. The ionic products of the other salts do not approach their solubility products. At pH higher than 9.0 the ionic product of $Mg(OH)_2$ will exceed the solubility product, and hence removal of CO_2 may result in precipitation of magnesium hydroxide as well as the carbonates.

Thompson and his co-workers (for example, Igelsrud and Thompson, 1936) have carried out extensive phase-rule studies of solutions containing some of the salts in sea water, but so far they have not extended their investigations to natural water.

Some indication of the great solubility of the major constituents is afforded by data on the separation of salts when sea water is frozen (p. 217). Somewhat similar data may be obtained from the evaporation studies by Usiglio (Thompson and Robinson, 1932), which again bring out the fact that sea water is far from saturated with most of the constituents.

TABLE 42

THE SOLUBILITY PRODUCTS OF CERTAIN SALTS IN DISTILLED WATER AND SEA WATER

(From Wattenberg and Timmermann, 1938)

Salt	K Distilled water	K' Sea water $S = 35\ ^0/_{00}$, $\vartheta = 20°$	Ionic product $Cl = 19.0\ ^0/_{00}$, $\vartheta = 20°$ pH = 8.2
$CaCO_3$	0.5×10^{-8}	50×10^{-8}	270×10^{-8}
$MgCO_3 \cdot 3H_2O$	0.1×10^{-4}	3.1×10^{-4}	0.14×10^{-4}
$SrCO_3$	0.3×10^{-9}	500×10^{-9}	39×10^{-9}
$Mg(OH)_2$	1×10^{-11}	5×10^{-11}	0.02×10^{-11}

The Oxidation-Reduction Potential of Sea Water

The oxidation-reduction potential is a measure of the ability of one chemical system to oxidize a second. It is generally expressed in volts relative to the normal hydrogen electrode. Those substances or solutions having high potentials are able to oxidize those with lower potentials. Although considerable work has been done on the oxidation-reduction potentials in living organisms, little is known about the conditions prevailing in the water. The potential in sea water has been considered by Cooper (1937a) to be associated only with the partial pressure of oxygen and the *p*H of the water. Under conditions of low oxygen content or when hydrogen sulphide is present, organic compounds dissolved in the water may have to be considered. The oxidizing or reducing conditions must be considered in two parts: namely, the *intensity* as expressed by the potential, and the *capacity*, or the poising of the system, which is a measure of the ability to oxidize or reduce a certain amount of material without significantly changing the potential. The poise of an oxidation-reduction system is somewhat analogous to the buffering capacity in hydrogen ion concentration. The oxidation-reduction potential is generally determined electrometrically, although in certain cases special colorimetric indicators can be used (Michaelis, 1930, Hewitt, 1937).

The oxidation-reduction potential of the environment is important to organisms. So-called aerobic bacteria thrive at a higher potential than micro-aerophiles, and anaerobic bacteria can exist only when the potential is low. Hence, in stagnant water and muds where there is no oxygen and the potential is low, only anaerobic forms can exist. The potential is also of geological importance, as the character of certain of the constituents of the sediments will be determined by the prevailing "oxidizing" or "reducing" conditions (p. 996).

Inorganic Agencies Affecting the Composition of Sea Water

The factors that may modify the absolute and the relative concen, trations of the substances in sea water are exchange with the atmosphere- inflow of river water, freezing and melting of sea ice, and biological activity. Biological processes and their effects upon the distribution of various elements are considered in chapter VII.

Exchange with the Atmosphere. The distribution of salinity in the oceans, and hence the concentrations of the major elements, is maintained by agencies that are described elsewhere, but one point must be considered at this time. Over the sea and along its shores, spray is continually being swept up into the air, and as the spray represents actual particles of sea water with its dissolved salts, this process affords a mechanism for the removal of salts from the sea. A large portion of the spray undoubtedly falls back into the water or is carried down by rain (Köhler, 1921). However, winds blowing toward the land will carry with them their content of salt, which may be deposited on the land directly or carried down by the rain. Observations by Jacobs (1937) on the chloride content of the air near the sea showed concentrations ranging between 0.07 and 0.5 mg of chloride per cubic meter of air. The amount increased with the wind velocity and was greatest with onshore winds.

A considerable proportion of the dissolved material carried to the sea by rivers is "cyclic salt"—that is, salt that has been carried inland by the atmosphere and then deposited or carried down by rain and snow (Clarke, 1924, Knopf, 1931).

Besides the exchange of salts that takes place between the atmosphere and the ocean as described above, there is an exchange of dissolved gases and nitrogen compounds which may modify the quantity of these substances present in sea water that is in contact with the atmosphere. The factors that affect the exchange of gases are described elsewhere. The exchange of water between the atmosphere and oceans was taken up in chapter IV.

Rain water contains relatively high concentrations of nitrogen compounds, which are believed to be formed from the constituents of the atmosphere by electrical discharges; hence the atmosphere supplies to the ocean, either directly through rainfall or indirectly through run-off from the land, a certain amount of fixed nitrogen. Whether this increment in the amount of fixed nitrogen is balanced by deposition of organic nitrogen in sediments or by the liberation of gaseous nitrogen through the decomposition of nitrogen compounds in the sea is not yet known.

EFFECTS OF RIVERS ON THE COMPOSITION OF SEA WATER. The run-off from land is but a part of the cycle of leaching. The precipitation on the land contains only the cyclic salts, dissolved atmospheric gases, and nitrogen compounds. This water acts upon the rocks, contributing to the mechanical break-down of the solid material and extracting from them their more soluble constituents. The nature and quantity of the various elements dissolved depends upon the character of the rocks or soils with which the water comes in contact on its way to the sea. Because the leaching is carried out by water of low salt concentration yet relatively high in carbon dioxide compounds, it is capable of dissolving materials that would not pass into solution if they were in contact with sea water. In addition to dissolved material, rivers carry to the sea colloidal and particulate material in tremendous quantities. A considerable part of this debris is dropped to the sea bottom near shore, and much of the finer material coagulates and settles when mixed with sea water. Sea water reacts in various ways with the colloidal and finely dispersed material, and some of these reactions may affect the relative composition of the dissolved constituents. Interaction between the dissolved constituents of sea water and the sedimentary debris may be subdivided as follows: (1) solution of the constituents of the sediment, (2) adsorption on the sediment, (3) ionic exchange, and (4) reactions to form new substances. Little is known concerning the importance of these processes.

From the magnitude of the land area drained by rivers emptying into the sea and from the composition of the salts dissolved in river waters, Clarke (1924) has estimated that rivers contribute to the sea each year 2.73×10^9 metric tons of dissolved solids. By weighting the composition of the water of different river systems in proportion to the total supply of dissolved material, he obtained the average composition of river water shown in table 43. Comparison with the composition of the dissolved solids in sea water shows, when referred to the halides, that there is an excess of all of the substances reported. Hence, the effect of river waters will be to modify the relative composition of the dissolved solids in sea water. Possibly a relatively large proportion of the carbon dioxide and nitrate should be regarded as cyclic. In addition, it should be recalled that the cyclic sea salts, carried into the atmosphere as spray and then deposited or carried down by precipitation onto the land, will enter the compilation. If we assume that all of the chloride in the river water is cyclic, the amounts of the other elements must be modified in the proportions in which they occur in sea water. It is hardly possible that this assumption is entirely correct, but it may yield values that are closer to the truth. The average composition of river water adjusted in this way for cyclic salts is included in the table.

TABLE 43

PERCENTAGE COMPOSITION OF DISSOLVED SOLIDS IN RIVER AND SEA WATER

Ion	River water (weighted average)	Sea water	River water (less "cyclic" salts)
$CO_3^=$	35.15	0.41 (HCO_3^-)	35.13
$SO_4^=$	12.14	7.68	11.35
Cl^-	5.68	55.04	0.00
NO_3^-	0.90	.....	0.90
Ca^{++}	20.39	1.15	20.27
Mg^{++}	3.41	3.69	3.03
Na^+	5.79	30.62	2.63
K^+	2.12	1.10	2.02
$(Fe,Al)_2O_3$	2.75	.....	2.75
SiO_2	11.67	.....	11.67
Sr^{++}, H_3BO_3, Br^-	.....	0.31	.....
	100.00	100.00	89.75

It is not known whether the addition of dissolved solids brings about progressive changes in the relative composition of the sea salts or whether there is any progressive alteration of the total salt content or salinity. In any event, both processes must be exceedingly slow. The total amount of dissolved solids contributed by the rivers each year is only an infinitesimal fraction, 5.4×10^{-8}, of the total dissolved solids in the ocean.

Even this small fraction does not represent a net gain, as there are many processes which remove material from solution. Certain elements accumulate in the marine sediments and are precipitated either through physical reactions or by biological activity. This is particularly true of the calcium and magnesium carbonate which form calcareous deposits and of the silicon which is found in organic siliceous deposits (radiolarian and diatom oozes). The sodium and potassium may be removed from solution by adsorption on, or ionic exchange with, the clay particles brought to the sea by rivers. However, in the latter case some other element will be released to the water in equivalent amounts. Other aspects of this problem are considered in connection with marine sediments and geochemistry, but it must be admitted that most questions related to changes in composition of sea water are still unsolved. In dealing with these it must also be considered that the amount of water may be changing. Essentially, all the river water is cyclic, but it is known that juvenile water of subterranean origin is continually being added to the surface water. In addition, the amount of water represented by the ice caps may be variable. Goldschmidt (1933) has estimated that for each square centimeter of the earth's surface there are 273 l of water subdivided as follows:

Sea water	268.45	l
Fresh water	0.1	"
Continental ice	4.5	"
Water vapor	0.003	"

The average composition of the river water is of interest in considering the effect on the oceans as a whole and over long periods, but particular investigations must be concerned with the effects brought about by individual rivers whose dissolved solids may differ markedly in composition and concentration from the average. Data can be obtained from Clarke (1924) or similar sources; as an illustration, values for several of the large American rivers are given in table 44.

From these examples it can be seen that the composition of individual rivers may differ considerably from the average. Thus, the Columbia River is low in chloride and the Colorado River is high, and the latter river is high in sodium and sulphate and below average in calcium and carbonate. The effect that dilution will have upon the chlorosity factors will therefore depend upon the character of the river water.

Thus far we have considered only the more abundant elements in the river water. Undoubtedly, all elements are carried to the sea either in solution or as finely divided particulate material. The high production of plant and animal life which frequently occurs near the mouths of rivers has sometimes been ascribed to the plant nutrients introduced by the rivers. Riley (1937) has found that the Mississippi

River water contains higher concentrations of phosphate and nitrogen compounds than the surface sea water in the Gulf of Mexico, and that this has a direct effect upon the amount of life in the waters off the mouth of the river. From studies in the English Channel, Atkins (1923) concluded, on the other hand, that the river water had little effect upon the immediate production, as most of the nutrients were used up by organisms living in the rivers.

Effects of Formation and Melting of Sea Ice on the Composition of Sea Water. A laboratory study of the freezing of sea water was made by Ringer, whose results have been reported by Krümmel (1907) and Johnstone (1928). In these experiments sea water was cooled in the laboratory, and at various temperatures below the initial freezing point the ice and precipitated salts were separated from the mother liquor. Sea water of salinity $35.0\ ^0/_{00}$ begins to freeze at −1.91°C (p. 66). At first, pure ice crystals separate, and, as the concentration of the brine is increased, the temperature must be further reduced to bring about the formation of additional ice. As the temperature is lowered and the concentration of the brine is increased, the solubility of certain of the dissolved salts is exceeded. At −8.2° the Na_2SO_4 begins to separate and continues to do so with further cooling. At −23° the NaCl begins to crystallize. In addition, a certain amount of $CaCO_3$ precipitates. Ringer's analyses of the "ice" (including the ice crystals and the precipitated salts) and the brine when the temperature had been reduced to −30° are as follows:

Table 44

PERCENTAGE COMPOSITION OF DISSOLVED SOLIDS IN RIVER WATERS
(Data from Clarke, 1924)

Ion	Average	Mississippi River	Columbia River	Colorado River
$CO_3^{=}$	35.15	34.98	36.15	13.02
$SO_4^{=}$	12.14	15.37	13.52	28.61
Cl^-	5.68	6.21	2.82	19.92
NO_3^-	0.90	1.60	0.49	....
Ca^{++}	20.39	20.50	17.87	10.35
Mg^{++}	3.41	5.38	4.38	3.14
Na^+	5.79	8.33*	8.12	19.75
K^+	2.12		1.95	2.17
$(Fe,Al)_2O_3$	2.75	0.58	0.08	....
SiO_2	11.67	7.05	14.62	3.04
Annual contribution of dissolved solids (metric tons)		100,000,000	19,000,000	13,416,000
Salt content (g/l)		0.166	0.0924	0.702

* Sum.

One kilogram of sea water, initial salinity 35.05 $^{0}/_{00}$, yielded:

Ice crystals	931.9 g
NaCl crystals	20.23 “
Na_2SO_4 crystals	3.95 “
$CaCO_3$ crystals	Trace
Brine	43.95 “

The brine contained 23.31 g of H_2O and

Na^+	1.42 g	Cl^-	7.03 g
Mg^{++}	1.31 “	Br^-	0.08 “
K^+	0.38 “	$SO_4^=$	0.03 “
Ca^{++}	0.39 “		

From these data it is readily seen that, when the temperature of the ice and brine is lowered to −30°, there are marked differences in the relative composition of the salts in the "ice" and in the brine. If the cooling is continued to −50°, there is further separation of ice and salt crystals, but some very concentrated brine is still present.

From these experiments it would appear that the formation of sea ice *might* have a pronounced effect upon the relative composition of the salts in the water. The brine from which it formed would be modified in one direction, and, if melting took place in water other than that from which the ice formed, the effect would be in the opposite direction. However, the formation of sea ice in nature is not reproduced by these laboratory experiments. Let us suppose that, in a region where the depth to the bottom is moderate or great, sea water of normal composition is subjected to cooling at the surface. The resulting increase in density gives rise to convection movements that continue until the water at the surface reaches the freezing point, and then ice will begin to form. The brine, being of greater concentration but having virtually the same temperature, will sink and new water will be brought toward the surface and into contact with the ice. At first, isolated, elongated ice crystals are produced, but as the freezing continues these form a matrix in which a certain amount of the brine is mechanically included. The ice crystals themselves are at this stage probably "pure ice." If the freezing proceeds rapidly, the brine will accumulate in separate cells within the body of the ice and, as the temperature of the ice near the surface is reduced, more ice crystals are formed, the cells decrease in size, and the concentration of the brine in the cells increases (fig. 16, p. 72). This may continue so far that solid salts crystallize in the cells. From this it can be seen that there is not necessarily any relative change in the composition of the dissolved salts in the sea water and in the sea ice (ice crystals plus the enclosed brine).

The salinity of the ice, using the same definition as applied to sea water, has been shown to depend upon the rate of freezing. Malmgren (1927), from the observations made by the *Maud* Expedition, gives the following average values showing the relation between the salinity of new ice and the air temperature, where the latter is used as a measure of the rate of freezing.

Air temperature (°C)	*Salinity of ice* ($^0/_{00}$)
−16	5.64
−28	8.01
−30	8.77
−40	10.16

The salinities are based upon chlorinity determinations made on samples of the melted ice. The salinity of the surface water was about 30 $^0/_{00}$. The effect of the rate of freezing is also shown by the analyses of samples obtained in April from an ice floe that had started to form the preceding November:

Distance from surface of ice (cm)	0	6	13	26	45	82	95
Salinity of ice ($^0/_{00}$)	6.74	5.28	5.31	3.84	4.37	3.48	3.17

The lower salt content of the deeper ice is related to the slower rate of formation. When ice is formed with extreme rapidity, its salinity will approach that of the water from which it is produced.

According to Ringer's experiments the cooling of ice containing cells of brine leads to formation of additional ice crystals and, if the temperature is reduced sufficiently, to separation of salt crystals within the ice. With very rapid freezing, brine and salt crystals may accumulate on the surface of the ice, making the surface "wet" at temperatures of −30° to −40°C and greatly increasing the friction against sled runners or skis.

In such rapidly frozen ice the cells containing the brine are large or numerous. If the temperature rises, the ice surrounding the cells melts and the separated salt crystals are dissolved, but before complete solution has taken place the brine cells may join, permitting the brine to trickle through the ice. Under these conditions some of the solid salts may be left in the ice, and the composition of the water obtained by melting will differ from that of normal sea water. If, on the other hand, the temperature of the ice is raised to 0°C, all salts dissolve, the cells grow so large that the ice becomes porous, all brine trickles down from the portions of the ice above the sea surface, and the exposed old ice becomes fresh and can be used as a source of potable water.

Analyses by Wiese (1930) indicate that the processes that have been described may be effective in changing the relative composition of the salts. He found that the sulphate and alkalinity factors were greater in the ice than in the water and were greater in old ice than in newly frozen ice. This indicates that small amounts of sulphate, probably present as Na_2SO_4, have remained in the ice during the process of ageing and, probably, that the relative amounts of $CaCO_3$ have changed.

Results of the *Maud* Expedition, reported by Malmgren (1927) and Sverdrup (1929), are not in agreement with the findings of Wiese. Chlorinities of water obtained by melting ice were systematically higher when determined by titration than when computed by means of Knudsen's Hydrographical Tables from observations of density. This discrepancy was interpreted to mean that the sea ice contains an excess of chlorides, but it may arise from the application of Knudsen's Tables to water that has been diluted by essentially distilled water, as explained on p. 59. The fact that the SO_4/Cl ratio was nearly the same in the ice and the sea water (Malmgren, 1927, p. 9) supports the latter explanation and indicates that no changes in relative concentration had resulted from processes of freezing and melting. The problem, however, cannot be considered solved, and it offers opportunities for further laboratory investigations and observations in the field.

Geochemistry of the Ocean Waters

The total quantity of dissolved solids present in the waters of the oceans can be estimated by assuming an average salinity of 35 $^0/_{00}$ and assuming that the volume of the ocean is 1.37×10^9 km^3 (p. 15). With a density *in situ* of 1.04 for the ocean waters, the dissolved solids amount to 5×10^{16} metric tons. This immense quantity of material would form a layer of dried salts 45 m thick over the entire earth, or 153 m thick over the present land area. The amount in tons of any element may be estimated by multiplying the value given in the first column in table 45 by 1.42×10^{12}. The figures for the variable elements correspond to the higher values listed in table 36. Obviously the total amounts of even the trace elements are tremendous, and, if methods of extraction were economically feasible, the oceans would serve as an "inexhaustible" source of these substances.

According to present theories, most of the solid material dissolved in the sea originated from the weathering of the crust of the earth. The problem as to the amount of rock weathered has been treated by Goldschmidt (1933) in the following way. For each square centimeter of the surface of the earth there are 278 kg of sea water; therefore, for each square centimeter the ocean water contains very nearly 3 kg of sodium. The average sodium content of igneous rocks is 2.83 per cent, and in sedimentary deposits it is 1.00 per cent. In the process of weathering, a certain amount of the material is leached away, and Goldschmidt estimates that the mass of the sedimentary deposits (Y) is 0.97 of the original igneous rocks (X) that gave rise to them. Therefore,

$$Y = 0.97X, \qquad \text{and} \qquad 2.83X - 1.00Y = 100 \times 3.00.$$

From this we find that for each square centimeter of the earth's surface about 160 kg of igneous rocks have been weathered. Therefore, approxi-

TABLE 45

ELEMENTS IN SEA WATER AND IN THE EARTH'S CRUST

Element	Sea water $S = 35^0/_{00}$ (mg/kg)	Potential "supply" in 600 g of rock (mg/kg of sea water)	Percentage in solution
Silicon	4	165,000	0.002
Aluminum	0.5	53,000	0.001
Iron	0.02	31,000	0.0001
Calcium	408	22,000	1.9
Sodium	10,769	17,000	65
Potassium	387	15,000	2.6
Magnesium	1,297	13,000	10
Titanium	....	3,800	?
Manganese	0.01	560	0.002
Phosphorus	0.1	470	0.02
Carbon	28	300	9
Sulphur	901	300	300
Chlorine	19,353	290	6700
Strontium	13	250	5
Barium	0.05	230	0.02
Rubidium	0.2	190	0.1
Fluorine	1.4	160	0.9
Chromium	p	120	?
Zirconium	....	120	?
Copper	0.01	60	0.02
Nickel	0.0001	60	0.0002
Vanadium	0.0003	60	0.0005
Tungsten	....	41	?
Lithium	0.1	39	0.2
Cerium	0.0004	26	0.002
Cobalt	p	24	?
Tin	p	24	?
Zinc	0.005	24	0.02
Yttrium	0.0003	19	0.002
Lanthanum	0.0003	11	0.003
Lead	0.004	10	0.04
Molybdenum	0.0005	9	0.005
Thorium	<0.0005	6	0.01
Cesium	0.002	4	0.05
Arsenic	0.02	3	0.7
Scandium	0.00004	3	0.001
Bromine	66	3	2000
Boron	4.7	2	240
Uranium	0.015	2	0.8
Selenium	0.004	0.4	1
Cadmium	p	0.3	?
Mercury	0.00003	0.3	0.001
Iodine	0.05	0.2	25
Silver	0.0003	0.06	0.5
Gold	0.0_56	0.003	0.3
Radium	0.0_93	0.0_66	0.05

p = present

mately 600 g of rock have been weathered for each kilogram of water in the oceans. Of the total sodium, 65 per cent has accumulated in the sea water and 35 per cent has been deposited in sedimentary rocks. The 600 g of igneous rock have been, therefore, a potential supply of the constituent elements to the sea, although in most cases only a part of the material has actually dissolved or *remained* in solution. Using 600 g as the amount of rock weathered and following Goldschmidt's estimate (1937) of the composition of the earth's crust, the "supply" of elements listed in table 45 is obtained. A number of the minor constituents of rocks are not included in this tabulation. The "percentage in solution" has been obtained by dividing the amount of each element present in sea water by the potential supply. This procedure has been followed by Goldschmidt (1937).

Examination of table 45 shows that the elements may be grouped in three classes, depending upon the percentage in solution: (1) Sulphur, chlorine, bromine, and boron occur in amounts greater than those which could have been supplied by the weathering of the 600 g of rock. Goldschmidt considers that these elements were present in the primeval atmosphere as volatile compounds and that they accumulated in the ocean waters in the earliest times. (2) Calcium, sodium, potassium, magnesium, carbon, strontium, selenium, and iodine, which form relatively soluble compounds, are present in sea water in amounts greater than 1 per cent of the potential supply. (3) The remaining elements, which are present in small amounts.

It is striking that silicon, aluminum, and iron, the most abundant elements in igneous rocks (oxygen is actually the most abundant, but does not have to be considered here), are present in sea water in extremely small amounts. Thus, the relative abundance of the elements in sea water differs markedly from that in the earth's crust. With a few exceptions, all of the elements have been potentially available in much larger amounts than are actually present in solution. The relative composition of river water differs from that of sea water, and, in addition to the dissolved constituents, rivers introduce large quantities of particulate material that would pass into solution if the sea water were unsaturated with respect to these substances. Therefore, it appears that factors operating in the sea itself must control the concentrations of many of the elements that are potentially available in large amounts. These factors are solubility, physical-chemical reactions, and biological activity. Our present knowledge is inadequate to designate which process or processes may control the concentration of a given element. Therefore, the following remarks will merely indicate the character of the factors that may be involved.

Certain elements may be present in such amounts that the solubility of their compounds may limit their concentration. In these cases, additional amounts brought to the sea in solution by rivers will be removed by chemical precipitation. The quantities of other elements may be controlled by physical-chemical processes that are, however, more complex than the precipitation of some simple salt—for example, the reactions which may take place between the dissolved substances and the colloidal and particulate material introduced by rivers. Included among such processes are ionic adsorption, base exchange, and the formation of complex minerals. Such reactions may remove from solution ions that would not be precipitated in absence of colloidal or particulate material. Biological activity is undoubtedly of great importance in controlling the concentrations of many of the elements in the sea. Cyclical processes, in which elements are removed from solution but are later released by metabolic activity, need not be considered. However, a certain amount of the material built up by organisms falls to the sea bottom, becomes a permanent part of the deposits, and is therefore removed from solution. The concentration of elements carried down in this way may be considered to be at least partly controlled by the activity of marine organisms. The character of the skeletal structures and of the detrital organic matter deposited in this way is discussed in chapters VII and XX. Organisms remove from solution elements that would not otherwise precipitate, and, if conditions are such that some of this material becomes a permanent part of the sediments, it is obvious that biological activity must play an important part in controlling the composition of the water. Not only the major constituents of skeletal structures such as calcium, carbon, silicon, and so on, but nitrogen, phosphorus and many elements present in the sea in small concentrations are also accumulated by marine organisms.

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