### CHEMISTRY OF SEA WATER

## **Introduction** and Composition

## Introduction

Oceanography is the branch of science dealing with oceans. Oceanography is not a single science but rather a combination of various sciences. Chemistry occupies a central position among other sciences in understanding oceanography. In the field of physical oceanography, the knowledge of the water masses of oceans and their origin is largely based on measurements of chemical parameters such as salinity and  $Co_2$  content. Chemical studies are also important to geologists in explaining the models of formation of mysterious manganese nodules and phosphate nodules which grow on the ocean floor. Determination of nutrients especially micro-nutrient elements (like N,P) are of great importance to marine biologists concerned with fertility of the sea. Therefore to truly understand the ocean and how it work, one should know about almost all fields of sciences and their relationships to the marine environment. oceanography is divided into 4 main parts as

- i. Chemical oceanography
- ii. Biological oceanography
- iii. Physical oceanography
- iv. Geological oceanography
- In this unit the following topics will be covered.
- 1. Chemsitry of sea water
- 2. Constancy of composition
- 3. Elements present in sea water
- 4. Artificial sea water
- 5. Dissolved gases in sea water
- 6. CO<sub>2</sub> system and <u>alkalinity</u>
- 7. Inorganic agencies affecting composition of sea water

#### Chemistry of sea water

Seawater is a complex mixture of 96.5% water, 2.5% salts, and small amounts of other substances. chemical formula for water is H2O and for salt NaCl.Chemical formula for water is H2O. Its atomic weight is 18.Chemical formula of salt depends on the compounds or elements under going reaction when producing a saltcommon salts are Sodium chloride.

#### **Properties of sea water**

Seawater properties are different from pure water seawater has the following properities.

- 1. High density and specific gravity
- 2. Depression in freezing point
- 3. Elevated boiling point
- 4. Higher osmotic pressure
- 5. Good conductor of electricity

## **Properties of seawater**

Sea water is a mixture of 96.5% pure water and 3.5% other material such as salts, dissolved gases, organic substances, and undissolved particles. Its physical properties are mainly

determined by the 96.5% pure water. The physical properties of pure water will therefore be discussed first.

Pure water, when compared with fluids of similar composition, displays most uncommon properties. This is the result of the particular structure of the water molecule  $H_2O$ : The hydrogen atoms carry one positive charge, the oxygen atom two negative charges, but the atom arrangement in the water molecule is such that the charges are not neutralized the charges would be neutralized if the angle were  $180^{\circ}$  rather than  $105^{\circ}$ .

The major consequences of the molecular structure of pure water are:

- The water molecule is an electric dipole, forming aggregations of molecules (polymers), of on average six molecules at 20°C. Therefore, water reacts slower to changes than individual molecules; for example the boiling point is shifted from -80°C to 100°C, the freezing point from -110°C to 0°C.
- 2. Water has an unusually strong disassociative power, i.e. it splits dissolved material into electrically charged ions. As a consequence, dissolved material greatly increases the electrical conductivity of water. The conductivity of pure water is relatively low, but that of sea water is midway between pure water and copper. The angle 105° is close to the angle of a tetrahedron, i.e. a structure with four arms emanating from a centre at equal angles (109° 28'). As a result, oxygen atoms in water try to have four hydrogen atoms attached to them in a tetrahedral arrangement. This is called a "hydrogen bond", in contrast to the (ionic) molecular bond and covalent bonding. Hydrogen bonds need a bonding energy 10 to 100 times smaller than molecular bonds, so water is very flexible in its reaction to changing chemical conditions.
- 3. Tetrahedrons are of a more wide-meshed nature than the molecular closest packing arrangement. They form aggregates of single, two, four and eight molecules. At high temperatures the one and two molecule aggregates dominate; as the temperature falls the larger clusters begin to dominate. The larger clusters occupy less space than the same number of molecules in smaller clusters. As a result, the density of water shows a maximum at 4°C.

Physical properties of most substances show uniform variation with temperature. In contrast, most physical properties of pure water show a minimum at some intermediate temperature. Sound velocity shows a maximum at  $74^{\circ}C$ 

A list of some minimum temperatures		
The physical property is given first, followed by the temperature in $^{\circ}C$ at which the minimum occurs.		
oxygen solubility	80 <sup>0</sup> C	
specific volume	4 <sup>0</sup> C	
specific heat	34 <sup>0</sup> C	
hydrogen solubility	37 <sup>0</sup> C	
compressibility	44 <sup>0</sup> C	
speed of light	-1 <sup>0</sup> C	

speed of sound ( maximum )	74 <sup>0</sup> C
----------------------------	-------------------

When freezing, all water molecules form tetrahedrons. This leads to a sudden expansion in volume, ie a decrease in density. The solid phase of water is therefore lighter than the liquid phase, which is a rare property. consequences are:

# 1. The Concept of Salinity

Sea water contains 3.5% salts, dissolved gasses, organic substances and undissolved particulate matter. The presence of salts influences most <u>physical properties of sea water</u> like density, compressibility, freezing point, temperature of the density maximum to some degree but does not determine them. properties like viscosity, and light absorbtion) are not significantly affected by salinity. Particle and dissolved matter do affect light absorption in sea water and this influence is used in most optical applications. Two properties which are determined by the amount of salt in the sea are conductivity and osmotic pressure.

Ideally, salinity should be the sum of all dissolved salts in grams per kilogram of sea water. In practice, this is difficult to measure. The observation that - no matter how much salt is in the sea the various components present in a fixed ratio, helps to overcome the difficulty. It allows determination of salt content through the measurement of a substitution quantity and <u>calculation</u> of the total of all material making up the salinity from that measurement.

Determination of salinity could thus be made through its most important component, chloride. Chloride content was defined in 1902 as the total amount in grams of chlorine ions contained in one kilogram of sea water if all the halogens are replaced by chlorides. The definition reflects the chemical titration process for the determination of chloride content and is still of importance when dealing with historical data.

Salinity was defined in 1902 as the total amount in grams of dissolved substances contained in one kilogram of sea water if all carbonates are converted into oxides, all bromides and iodides into chlorides, and all organic substances oxidized. The relationship between salinity and chloride was determined through a series of fundamental laboratory measurements based on sea water samples from all regions of the <u>world ocean</u> and was given as

# $S(^{\circ}/_{oo}) = 0.03 + 1.805 \text{ Cl}(^{\circ}/_{oo})$

The symbol  $^{\circ}/_{oo}$  stands for "parts per thousand" or "per ml"; a salt content of  $3.5\%^{0}$  is equivalent to  $35\%_{oo}$ , or 35 grams of salt per kilogram of sea water.

The fact that the equation of 1902 gives a salinity of 0.03  $^{\circ}/_{\circ\circ}$  for zero chlorinity is a cause for concern. It indicates a problem in the water samples used for the laboratory measurements. The United Nations Scientific, Education and Cultural Organization (UNESCO) decided to repeat the base determination of the relation between chlorinity and salinity and introduced a new definition, known as absolute salinity,

S ( $^{\circ}/_{\circ\circ}$ ) = 1.80655 Cl ( $^{\circ}/_{\circ\circ}$ ) (1969)

The definitions of 1902 and 1969 give identical results at a salinity of 35  $^{\circ}/_{\circ\circ}$  and do not differ significantly for most applications.

The definition of salinity was reviewed again when techniques to determine salinity from measurements of conductivity, temperature and pressure were developed. Since 1978, the "<u>Practical</u> Salinity Scale" defines salinity in terms of a conductivity ratio:

" The <u>practical</u> salinity, symbol S, of a sample of sea water, is defined in terms of the ratio K of the electrical conductivity of a sea water sample of 15°C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 0.0324356, at the same temperature and pressure. The K value exactly equal to one corresponds, by definition, to a <u>practical</u> salinity equal to 35." The corresponding formula is:  $S = 0.0080 - 0.1692 \text{ K}^{1/2} + 25.3853 \text{ K} + 14.0941 \text{ K}^{3/2} - 7.0261 \text{ K}^2 + 2.7081 \text{ K}^{5/2}$ 

Note that in this definition, salinity is a ratio and  $\binom{0}{00}$  is therefore no longer used, but an old value of  $35^{\circ}/_{00}$  corresponds to a value of 35 in the <u>practical</u> salinity. Some oceanographers

cannot get used to numbers without units for salinity and write "35 psu", where psu is meant to stand for "<u>practical</u> salinity unit". As the <u>practical</u> salinity is a ratio and therefore does not have units, the unit "psu" is rather meaningless and strongly discouraged. Again, minute differences occur between the old definitions and the new <u>Practical</u> Salinity Scale, but they are usually negligible.

# **Electrical Conductivity of seawater:**

The conductivity of sea water depends on the number of dissolved ions per volume (i.e. salinity) and the mobility of the ions (ie temperature and pressure). Its units are mS/cm (milli-Siemens per centimetre). Conductivity increases by the same amount with a salinity increase of 0.01, a temperature increase of 0.01°C, and a depth (ie pressure) increase of 20 m. In most <u>practical</u> oceanographic applications the change of conductivity is dominated by temperature.

# Density

Density is one of the most important parameters in the study of the oceans' dynamics. Small horizontal density differences (caused for example by differences in surface heating) can produce very strong currents. The determination of density has therefore been one of the most important tasks in oceanography. The symbol for density is the Greek letter  $\rho$  (rho).

The density of sea water depends on temperature T, salinity S and pressure p. This dependence is known as the Equation of State of Sea Water .

The equation of state for an ideal gas was given by

# $p = \rho R T$

where R is the gas constant. The exact equation for the entire range of temperatures, salinities and pressures encountered in the ocean

# $\rho = \rho(T, S, p)$

(where *S* is salinity) is the result of many careful laboratory determinations. The first fundamental determinations to establish the equation were made in 1902 by Knudsen and Ekman. Their equation expressed  $\rho$  in g cm<sup>-3</sup>. New fundamental determinations, based on data over a larger pressure and salinity range, resulted in a new density equation, known as the "International Equation of State (1980) ". This equation uses temperature in °C, salinity from the <u>Practical</u> Salinity Scale and pressure in dbar (1 dbar = 10,000 pascal = 10,000 N m<sup>-2</sup>) and gives density in kg m<sup>-3</sup>. Thus, a density of 1.025 g cm<sup>-3</sup> in the old formula corresponds to a density of 1025 kg m<sup>-3</sup> in the International Equation of State.

Density increases with an increase in salinity and a decrease in temperature, except at temperatures below the density maximum. Oceanic density is usually close to 1025 kg m<sup>-3</sup> (In freshwater it is close to 1000 kg m<sup>-3</sup>). Oceanographers usually use the symbol  $\sigma_t$  (the Greek letter sigma with a subscript t) for density, which they pronounce "sigma-t". This quantity is defined as  $\sigma_t = \rho$  - 1000 and does not usually carry units (it should carry the same units as  $\rho$ ). A typical seawater density is thus  $\sigma_t = 25$ . A useful rule of thumb is that  $\sigma_t$  changes by the same amount if *T* changes by 1°C, *S* by 0.1, and *p* by the equivalent of a 50 m depth change.

Notice that the density maximum is above the freezing point for salinities below 24.7 but below the freezing point for salinities above 24.7. This affects the thermal convection:

- S < 24.7: The water cools until it reaches maximum density; then, when the surface water becomes lighter (ie after the density maximum has been passed) cooling is restricted to the wind-mixed layer, which eventually freezes over. The deep basins are filled with water of maximum density.
- S > 24.7: Convection always reaches the entire water body. Cooling is slowed down because a large amount of heat is stored in the water body. This is because the water reaches freezing point before the maximum density is attained.

If your browser supports JavaScript you can check the range of seawater density and its dependence on temperature and salinity at surface pressure with this density calculator: Enter a value for temperature, a value for salinity and press the calculate button. Verify your result against the appropriate TS-diagram.

## **Composition of sea water**

As water is a good solvent most elements on the <u>earth</u> are found dissolved in sea water of the 108 elements discovered so for 84 elements have been found to be in seawater.

The major constituents comprise about 99.7% of all dissolved materials. The remaining 0.3% comprises of the three categories of dissolved gases, nutrients and trace elements. The concentrations of dissolved gases, nutrients, and trace elements are greatly affected by biological organisms, the climate, and some geochemical processes. Their concentrations are varying so much from place to place and from time to time. As a very rough approximation, the dissolved gases are generally one or two hundred times more abundant that the nutrients, and the nutrients, in turn, are thousands of times more abundant than are trace elements.

In addition to what is in solution seawater also contains some fine particulate matter in suspension. Some of this particulate matter will eventually dissolve, and some will eventually add to the sediment on the ocean bottom. Organic particulate matter has other possible fates. It may be consumed directly by organisms or it may decompose through bacterial action and return to solution as nutrients, reusable by plants in photosynthesis.

The suspended particulate matter has a noticeable effect on the seawater chemistry. The particles may exchange some of their cations or anions with those dissolved in the water. They also provide surfaces on which some dissolved materials may precipitate out of solution and from which other materials may be dissolved into solution. The composition are conveniently grouped into four broad categories.

- a. Major constituents
- b. Dissolved gases
- c. Nutrients or disslolved organic matter
- d.Trace elements

# **Dissolved components of Sea water**

A.Major constituents

According to cuckin (1968) major constituents are those which makes a significant contribution to measure salinity. wilson (1975) clssified major constituents as the elements present ar concentration graterthan 1ppm/1mg/kg.major constituents comprise about 99.7% of all the dissolved materials.

Ion	Concentration		Percent
	g/kg	mM <sup>a</sup>	rree ion
Cl	19.354	558	100
Na <sup>+</sup>	10.77	479	98
Mg <sup>++</sup>	1.290	54.3	89
SO <sub>4</sub>	2.712	28.9	39

Major dissolved components of Sea water for a salinity of 35%

Ca <sup>++</sup>	0.412	10.5	88
$\mathbf{K}^+$	0.399	10.4	98
HCO <sub>3</sub> <sup>-b</sup>	0.12	2.0	80

A.1. Primary are Cl<sup>-</sup> (55.04%) and Na<sup>+</sup> (30.61%) which make up 85.65% of all the dissolved constituents.

2. Adding the next four most abundant major elements are  $(SO_4^{2-}, Mg^{2+}, Ca^{2+} \text{ and } K^+)$  which brings the total to >99% of the salts.

3. Finally the last five (HCO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, H<sub>3</sub>BO<sub>3</sub>, Sr<sup>2+</sup>, F<sup>-</sup>) brings the total to >99.99%.

4. Almost all of the 92 naturally occurring elements are found in the ocean.

5. Although the other components are a very small % of the dissolved materials they are essential for life on  $\underline{Earth}$ .

b. seven dissolved constituents, in order of decreasing abundance.

Constituent	0/00
Cl	19.2
Na <sup>+</sup>	10.7
SO4 <sup>2-</sup>	2.5
Mg <sup>2+</sup>	1.3
Ca <sup>2+</sup>	0.4
K <sup>+</sup>	0.4
HCO <sub>3</sub> -	0.1

<b>C.Other</b>	Elements	in	Seawater
----------------	----------	----	----------

	Element	Chemical Form	Average
			Concentration at
			35%
Ag	silver	AgCl <sup>-</sup> 2	25 pmol/kg <sup>+</sup> +
Al	Aluminium	$Al(OH)_4$	20nmol/kg
Ar	argon	Ar (gas)	
As	Arsenic	AsO <sub>4</sub> H <sup>2-</sup>	23nmol/kg
В	Boron	B(OH) <sub>3</sub>	0.42mmol/kg
Ba	Barium	Ba <sup>2+</sup>	100nmol/kg
Be	beryllium	BeOH <sup>+</sup> , Be(OH) $^{\circ}$ <sub>2</sub>	20 pmol/kg
Bi	Bismuth	${\rm BiO}^{+}$ , ${\rm Bi}({\rm OH})^{+}_{2}$	0.01-0.2 pmol/kg
Br	Bromine	Br⁻	0.84mmol/kg
С	Carbon	Co <sub>3+</sub> H <sup>-</sup> , organic C	2.3mmol/kg
Ca	Calcium	$Ca^{2+}$	10.3mmol/kg
Cd	Cadmium	CdCl ° 2	0.7nmol/kg
Ce	Cerium	$CeCO^{+}_{3}, Ce^{3+}, CeCl^{2+}$	20 pmol/kg

Cl	Chlorine	Cl <sup>-</sup>	0.546 mol/kg
Co	Cobalt	$\mathrm{Co}^{2+},\mathrm{Co}\mathrm{CO}_3^\circ$ , $\mathrm{Co}\mathrm{Cl}^+$	0.02nmol/kg
Cr	Chromium	CrO <sup>2-</sup> <sub>4</sub> , NaCrO <sub>4</sub>	4nmol/kg
Cs	Cesium	$Cs^+$	2.2nmol/kg
Cu	Copper	CuCo <sup>°</sup> <sub>3</sub> ,CuOH <sup>+</sup> , Cu <sup>2+</sup>	4nmol/kg
F	Fluorine	$F^{-}, MgF^{+}$	68 μ mol/kg
Fe	Iron	Fe(OH) ° 3	1 nmol/kg
Ga	Gallium	Ga(OH) <sub>4</sub>	?
Ge	Germanium	$Ge(OH)_4$ , $H_3Geo_4$	70 pmol/kg
Η	Hydrogen	$H_2O$	
He		He(gas)	
	helium		

### Dissolved gases in sea water

Gases in seawater include nitrogen  $(N_2)$ , Oxygen  $(O_2)$ , Carbon dioxide  $(CO_2)$ , hydrogen $(H_2)$ , and the noble gases argon(Ar),neon (Ne), and helium (He). Nitrogen and the three noble gases are inert (unreactive) and rarely involve directly in plant photosynthesis. In contrast, levels of dissolved  $(O_2)$  and  $(CO_2)$  are greatly influenced by photosynthesis and respiration of organisms. Therefore they vary greatly in space and time depending on the activities of plants and animals and are regarded as **non conservative**.

Gas	In Dry Air	In Surface	Water-Air
	(%)	Ocean Water	Ratio
		(%)	
Nitrogen (N <sub>2</sub> )	78.03	47.5	0:6
Oxygen(O <sub>2</sub> )	20.99	36.0	1:7
Carbon	0.03	15.1	5.03:3
dioxide(CO <sub>2</sub> )			
Argon (Ar),	0.95	1.4	1:5
hydrogen(H <sub>2</sub> ), neon			
(Ne) and helium			
(He)			

#### Trace elements in sea water

Trace elements are all chemical ingredients that occur in minute quantities in the ocean. Most trace elements, such as <u>manganese</u> (Mn), Lead (Pb), mercury (Hg), gold (Au), iodine(I), and iron (Fe), occur in concentrations of less than 1 ppm (part per million). Many occur in quantities of less than 1 part per billion (ppb) and even at 1 part per trillion. These low concentrations make certain trace elements difficult and sometimes even impossible to detect in seawater. However, despite their extremely low concentrations, trace elements can be critically important for marine organisms, Trace elements either help to promote life or kill life (toxicity).

List of	trace	Elements
---------	-------	----------

Trace Element	Concentration(ppb)*
Lithium(Li)	170
Iodine (I)	60
Molybdenum (Mo)	10
Zinc (Zn)	10

Iron (Fe)	10
Aluminium (Al)	10
Copper(Cu)	3
Manganese(Mn)	2
Cobalt (Co)	0.1
Lead (Pb)	0.03
Mercury (Hg)	0.03
Gold(Au)	0.004

\*ppb – Parts per billion

## Chapter 2: Constancy of composition and artificial seawater

## **Constancy of composition**

Salinity determinations from the world's oceans have revealed an important, findings that although salinity varies quite a bit because of differences in the total amount of dissolved salts, the relative proportions of the major constituents are constant. In other words the ratio of any two major constituents dissolved in seawater, such as  $Na^+/K^+$  or  $CI'/SO_4^{2^-}$ , is a fixed value, whether the salinity is 25, 30, 35%, or whatever. To put it in more familiar terms, let's imagine that the ratio of females to males in a populations is 1:4 (1 female for every 4 males) and that this ratio never changes regardless of population size. This means that the total number of people in the population can vary but the relative proportion of females to males does not change. In other words, the ratio of females to males is constant and is independent of population size. Just so, the ratio of any two major salt constituents in ocean water is constant and is independent of salinity. This is called constancy of composition.

This important discovery, made during the Glomar challenger expedition is termed the principle of constant proportion or constant composition, and was а major breakthrough in determining salinity of sea water in a rapid, accurate, and economical manner. In theory, all that need be done to quantify salinity is to measure the amount of only a single major ion dissolved in a sample of sea water, because all the other major constituents occur in fixed amounts relative to that ion. Chemists chose to measure Cl<sup>-</sup> for determining the salinity of sea water, because it is the most abundant solute in sea water and its concentration is easily determined. Actually, elements in the halogen family, which include chlorine, bromine, iodine, and fluorine, are difficult to distinguish analytically from one another. Therefore, chemists determine, not merely the Cl<sup>-</sup> content, but the chlorinity, tha is, the total quantity of halogens dissolved in water, expressed as g/kg (%). It is then simple matter to convert chlorinity to salinity by the given formula

Salinity (%)= 1.80655 x chlorinity (%)

Today, oceanographers rely on a variety of methods, including the electrical conductivity of sea-water, to make routine determinations of salinity.

## **Artificial seawater**

Artificial seawater of 33 ppt was prepared by dissolving 3.5 kg of seasalt crystals in 100 1 of fresh water along with 100 g of calcium chloride and 10 g of sodium bicarbonate. The next day the solution was filtered and the PH was adjusted to that of natural seawater with 0.1 N NaOH. Artificial seawater is used mostly for small aquarium research projects that need a highly repeatable and predictable seawater sources or inland systems where there is little choice. The advantage of artificial seawater is that it has a defined composition with reduced risk of chemical and biological contamination. Artificial seawater systems often work quite well, especially if operated very conservatively. However for some specialized

applications such as the hatchery phases of delicate organisms, there may be some problems due to complex interactions of seawater and organisms which are presently poorly understood (Huguenin and colt, 1989). Artificial seawater formulations that are useable with animals may not be suitable for plants.

# Chapter 3: Dissolved Gases in Sea water

## **Carbon Dioxide and Carbonate cycles**

Carbon dioxide has the most complicated behavior of all the gases in seawater. It occurs as a dissolved gas and in several other chemical forms. It is highly soluble in seawater. The carbondioxide enter the sea from the atmosphere and respiration of plants and animals in the ocean. When carbon dioxide (gas) dissolves, it forms a weak acid ( $H_2CO_3$ ), which acts as a buffer to stabilize the acidity of seawater. (Acidity is another way of expressing the abundance of hydrogen ions in water.)

Addition of acid ( $H^+$ ) creates more bicarbonate, which combines with acids to keep the acidity of the mixture unchanged. Thus respiration and decomposition processes producing carbon dioxide hardly affect the acidity of seawater, nor does removal of carbon dioxide during photosynthesis. Carbonate and bicarbonate freely give up and accept hydrogen ions in sea water, thus creating a buffer against sharp changes in acidity. Because of its complex chemical behavior, carbon dioxide is involved in many processes in the ocean.

# Alkalinity

Alkalinity or  $A_T$  is a measure of the ability of a solution to neutralize acids to the <u>equivalence</u> point of carbonate or bicarbonate. Alkalinity is closely related to the <u>acid neutralizing</u> capacity (ANC) of a <u>solution</u> and ANC is often incorrectly used to refer to alkalinity. The alkalinity is equal to the <u>stoichiometric</u> sum of the <u>bases</u> in solution. In the natural environment <u>carbonate alkalinity</u> tends to make up most of the total alkalinity due to the common occurrence and dissolution of <u>carbonate</u> rocks and presence of <u>carbon dioxide</u> in the atmosphere. Other common natural components that can contribute to alkalinity include <u>borate</u>, <u>hydroxide</u>, <u>phosphate</u>, <u>silicate</u>, <u>nitrate</u>, dissolved <u>ammonia</u>, the conjugate bases of some <u>organic acids</u> and <u>sulfide</u>.

## Theoretical treatment of alkalinity

In typical <u>groundwater</u> or <u>seawater</u> the measured alkalinity is set to be equal to:

 $A_{T} = [HCO_{3}^{-}]_{T} + 2[CO_{3}^{-2}]_{T} + [B(OH)_{4}^{-}]_{T} + [OH^{-}]_{T} + 2[PO_{4}^{-3}]_{T} + [HPO_{4}^{-2}]_{T} + [SiO(OH)_{3}^{-}]_{T} - [H^{+}]_{sws} - [HSO_{4}^{-}]$ 

(Subscript T indicates the total concentration of the species in the solution as measured. This is opposite to the free concentration, which takes into account the significant amount of <u>ion</u> <u>pair</u> interactions that occur in seawater.)

Alkalinity can be measured by titrating a sample with a strong acid until all the buffering capacity of the aforementioned ions above the pH of bicarbonate or carbonate is consumed. This point is functionally set to pH 4.5. At this point, all the bases of interest have been protonated to the zero level species, hence they no longer cause alkalinity. For example, the following reactions take place during the addition of acid to a typical seawater solution:

 $\begin{array}{l} HCO_{3}^{-} + H^{+} \rightarrow CO_{2} + H_{2}O \\ CO_{3}^{-2} + 2H^{+} \rightarrow CO_{2} + H_{2}O \\ B(OH)_{4}^{-} + H^{+} \rightarrow B(OH)_{3} + H_{2}O \\ OH^{-} + H^{+} \rightarrow H_{2}O \\ PO_{4}^{-3} + 2H^{+} \rightarrow H_{2}PO_{4}^{-} \\ HPO_{4}^{-2} + H^{+} \rightarrow H_{2}PO_{4}^{-} \end{array}$ 

# $[\operatorname{SiO(OH)_3}^-] + \operatorname{H}^+ \to [\operatorname{Si(OH)_4}^0]$

It can be seen from the above protonation reactions that most bases consume one proton ( $H^+$ ) to become a neutral species, thus increasing alkalinity by one per equivalent.  $CO_3^{-2}$  however, will consume two protons before becoming a zero level species ( $CO_2$ ), thus it increases alkalinity by two per mole of  $CO_3^{-2}$ . [ $H^+$ ] and [ $HSO_4^-$ ] decrease alkalinity, as they act as sources of protons. They are often represented collectively as [ $H^+$ ]<sub>T</sub>.

Alkalinity is typically reported as mg/l as  $CaCO_3$ . This can be converted into milliEquivalents per liter (mEq/l) by dividing by 50 (the approximate MW of  $CaCO_3/2$ ).

#### Factors influencing the composition of seawater

## Inorganic agencies affecting composition of sea water

Inflow of river water, freezing and melting of sea ice, biological activity and exchange of substances with the atmosphere are the factors which affect the <u>composition of sea</u> <u>water</u>. Along the shores, spray is swept up in to the air. Through this spray the dissolved salts in the water are removed from the sea to the atmosphere.

E.g. the chloride in the water are carried away in to the atmosphere. It is evidenced by the observation of chloride content in air near ocean in range between 0.07 and 0.5mg km of air. The exchange of dissolved gases and nitrogen compounds also modify the quantity of these substance in sea water.

### Effects of Rivers on the composition of sea water

Rivers contribute about 2.73 No<sup>9</sup> x 109 metric tons of dissolved solids. River water contains higher concentrations of phosphate and nitrogen compounds and it draws in to the sea. River also drains the leached out salts from the rock and highercarbondioxide compounds are also added by the rivers in to the sea. River water also adds ions like,  $CO_3$ , So<sub>4</sub>, Cl<sup>-</sup>, NO<sub>3</sub>, Ca<sup>++</sup>, mg<sup>++</sup>, Na<sup>+</sup>, K<sup>+</sup>, Sio<sub>2</sub>.

## Effects of formation and melting of sea ice:

Rivers contribute about 2.73 No<sup>9</sup> x 109 metric tons of dissolved solids. River water contains higher concentrations of phosphate and nitrogen compounds and it draws in to the sea. River also drains the leached out salts from the rock and higher carbondioxide compounds are also added by the rivers in to the sea. River water also adds ions like,  $CO_3^{-}$ So<sub>4</sub>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Ca<sup>++</sup>, mg<sup>++</sup>, Na<sup>+</sup>, K<sup>+</sup>, Sio<sub>2</sub>. The formation of ice has pronounced effect upon the relative composition of the salts in the water.