Soil And Water Chemistry

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Fisheries science holds the answers to the sustainability of aquatic life and the future of global food security.

Course Name	Soil and Water Chemistry
Lesson 1	Analytical Chemistry: Principles, Applications and Types
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Lesson 1

Objectives:

1. To understand the principles of different analytical chemistry techniques

2. To understand different analytical chemistry concepts

Glossary of terms:

Volumetry: Volumetry is measurement of volume of a solution of known concentration which is used to determine the concentration of the analyte.

Gravimetry: It is a technique through which the amount of an analyte (the ion being analysed) can be determined through the measurement of mass. Gravimetric analyses depend on comparing the masses of two compounds containing the analyte. The principle behind gravimetric analysis is that the mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

Standard solution: Standard solution is the one whose concentration or strength is accurately known. It is also sometimes referred to as “titrant”.

Titration: The Process of adding a standard solution from a volumetric burette to a solution of the unknown concentration in the conical flask until the reaction is just complete is known as “Titration”.

Indicator: The end point or equivalent point of titration is recognized with the help of a chemical reagent called “Indicator”.

Normality: It is a measure of concentration equal to the gram equivalent weight per litre of solution. Gram equivalent weight is the measure of the reactive capacity of a molecule. The solute's role in the reaction determines the solution's normality. Normality is also known as the equivalent concentration of a solution.

Molarity: It is a unit of concentration measuring the numbers of moles of a solute per litre of solution. Molarity is denoted with 'M'. A 1 M solution contains 1 mole of solute per litre of solution.

Molality: It is the number of moles of solute per kilogram of solvent. Solutions expressed in molal concentration are denoted with 'm'. 1 m solution contains 1 mole of solute per kilogram of solvent.

Formality: It is defined as the number of formula mass of any solute dissolved in one litre of solution. A solution is said to be one formal (1 F) if it contains one formula mass of the substance in one litre of solution.

Standard curve: A standard curve also known as Calibration curve, is a type of graph used as a quantitative research technique. Multiple samples with known concentration are measured and plotted on the graph, which then allows similar concentrations to be determined for unknown samples by interpolation on the graph. The samples with known concentration are the standards, and the graph is the standard graph.

Nomograph: These are graphical representations which are used by simply applying a straight edge across the plot through the points on scales representing independent variables, which then crosses the corresponding datum point for the dependent variable; the choice among independent and dependent variable is arbitrary so that each variable may be determined in terms of the others.

E-lecture:

1. What is Analytical Chemistry: Analytical chemistry is application of chemical knowledge for characterising the composition of matter, both qualitatively and quantitatively (the identification of matter under study is performed using qualitative analysis while quantitative analysis is used to determine how much (relative concentration or total amount) of the substance is present in the analyte . Methods used in analytical chemistry

are based on chemical and physical principles to study a substance which is to be analysed.

1.1 Classical methods of analytical chemistry:

A) Classical Qualitative methods: These methods can further be divided into

(a) Separation methods &

(b) Identification methods

(a) Separation methods:

i) Precipitation: This is a gravimetric method in which the reactants and products of a chemical reaction are used to analyse a substance. The metallic ions of many elements may enter into a reaction with the negative ions to form a new insoluble substance called the precipitate, which settles to the bottom of the solution. This is filtered out and washed.

ii) Extraction: This is a procedure in which a substance is removed from a matrix, both being in two immiscible phases. The most common technique for extraction of a compound from an aqueous solution is liquid-liquid extraction (LLE). Solid phase extraction (SPE) is a widely used method of sample preparation used to separate and enrich purified components from aqueous solution.

iii) Distillation: This is process of evaporation and condensation by which a component is separated out of a mixture of liquids. It is based upon the difference in boiling points or volatility between the various substances present in the mixture.

(b) Identification methods: These methods are based on colour, odour, melting and boiling points, radioactive or reactive properties of the analyte.

B) Classical Quantitative methods:

(a) Titration method: It includes acid-base or complexometric titration. Acid-base titration helps in quantifying an unknown acid or base in solution

by finding its concentration based on the exact amount of corresponding base or acid required to neutralize it. Complexometric titration is a volumetric analysis where end point of titration is the formation of a characteristic coloured complex, which is usually a metal complex.

(b) Gravimetric method: It uses precipitation or volatilization to determine the mass of the analyte from its ionic mass. Precipitation, Volatilization or electroanalytical methods are mostly used.

(c) Coulometric method: These methods help to determine the mass of matter transformed by electrolysis from the amount of electric current used or produced during the reaction.

1.2 Instrumental methods: Instrumental methods are mostly used in advance level of research and the same instrument may be used to separate, identify and quantify the analyte.

A) Instrumental separation methods:

(a) Chromatography: This method uses a mobile phase into which the mixture is introduced, which then passed through the stationary phase. Due to the different rates at which the components of the mixture travel through the stationary phase, they can be separated.

There are different types of chromatography:

(i) Paper or thin layer chromatography

(ii) Gas chromatography

(iii) Ion-exchange and size-exclusion chromatography

(iv) Reversed-phased chromatography, Two-dimensional chromatography, Hydrophobic interaction chromatography

Special Note

High Performance Liquid Chromatography (HPLC) is an advance technique in which the analyte is contained in a mobile phase passed through a stainless-steel column which is between 1 and 25 cm long and less than 1.0 mm to 4.6 mm internal diameter, filled tightly with micro size particles allowing the various components of a complex non-volatile mixture to separate rapidly. The final concentration is determined using computations based on the outputs at varying amounts of organic compound.

(b) Electrophoresis: In this method, an electric field is used to separate particles in a fluid because of development of a charged interface between them.

(c) Field Flow Fractionation: In this technique, a fluid suspension or solution is fed through a narrow channel and a field is applied right angles to it, causing the particles within the field to separate because of their varying mobility in response to the field force.

B) Instrumental qualitative and quantitative methods: These methods may utilize light, electromagnetic, heat and combinations of these to identify the analytes.

(a) Spectrometry: This method can isolate particles based on various properties like mass, momentum or energy. It includes techniques such as ion-mobility spectrometry based on mobility of ionised particles in a carrier gas, or mass spectrometry which measures the ratio of mass to charge of ions.

(b) Spectrophotometry: This method is based on Beer-Lambert law. Here a material or component is identified by its reflection or transmission of light, which depends on the wavelength. Visible, ultraviolet or near-infrared light may be used in this method. This method is widely used to study gases, solids or solutions.

Beer-Lambert Law

This law states that the absorbance of a light absorbing material is proportional to its concentration in solution. The general Beer-Lambert Law is usually written as

$$A = \varepsilon l c$$

Where

A is the measured absorbance

e is the *extinction coefficient* of the substance- unique for each substance

l is the sample path length measured in centimetres (i.e. the width of the cuvette almost always 1 cm)

c is the molar concentration of the solution (expressed in terms of molarity)

(c) Potentiometry: It is a method of analysis in which the concentration of an ion or substance is determined by measuring the potential developed when a sensitive electrode is immersed in the solution of the species to be determined. Commonly available pH meters are designed based on this principle.

(d) Conductometry: Conductometry is the measurement of the electrical conductivity of a solution. The main principle involved in this method is that the movement of the ions creates the electrical conductivity. The movement of the ions is mainly depended on the concentration of the ions. Electrical conductivity and Total Dissolved Solids (TDS) of water samples generally determined by instruments designed based on this principle.

(e) Turbidimetry/ Nephelometry: The principle of nephelometry and turbidimetry is based on the on the well-known law of Tyndall Effect. When light is passed through the suspension, part of incident radiant energy is dissipated by absorption, reflection, and refraction while remainder is transmitted. In fact the measurement of the intensity of transmitted light is a function of the concentration of dispersed phase and this becomes the basis of turbidimetric analysis.

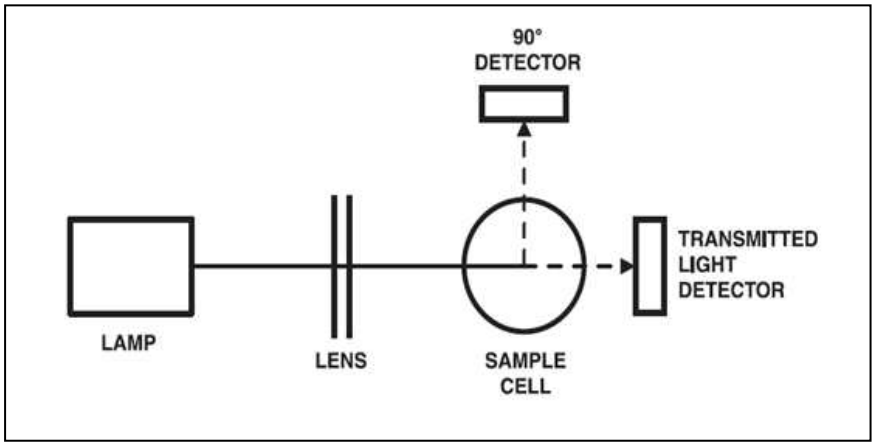

Fig.1. Schematic Diagram of a Nephelometer

(f) Radiometry: Radiometry is the science of measuring light in any portion of the electromagnetic spectrum. In practice, the term is usually limited to the measurement of infrared, visible, and ultraviolet light using optical

instruments. Irradiance is the intensity of light and is measured in watts per square meter.

1.3 Volumetry & Gravimetry:

A) Volumetry: It is a widely used quantitative analytical method. It involves measurement of volume of a solution of known concentration which is used to find out the concentration of the analyte.

Some of the widely used volumetric analysis are:

a) Acidimetry: The term acidimetry refers to that part of volumetric analysis whereby an acid solution at known concentration, along with a specific indicator, is used to titrate a base solution and thus work out its concentration.

b) Alkalimetry: The term alkalimetry refers to that part of volumetric chemical analysis which enables us to work out the concentration of an acid solution using an alkaline solution at a known concentration and a suitable indicator.

c) Argentometry: The determination of silver or halides by the precipitation of silver salts is known as argentometric titrations. The sample solution is titrated against a solution of silver nitrate of known concentration. It can be used for measurement of salinity.

B) Gravimetry: Gravimetric analysis is a technique through which the amount of an analyte (the ion being analysed) can be determined through the measurement of mass. Gravimetric analyses depend on comparing the masses of two compounds containing the analyte.

Principle: Mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

For an accurate gravimetric analysis, the following 3 conditions must be met:

i) The ion being analysed must be completely precipitated.

ii). The precipitate must be pure compound.

iii) The precipitate must be easily filtered.

1.4 Standard Solutions: A solution whose strength or concentration is accurately known is referred to as Standard solution.

i) The most accurate and convenient way of preparing a standard solution is to weigh the reagent, dissolve it, and dilute the solution to a definite volume in a volumetric flask. However, this method can only be used if the reagent is a primary standard.

ii) In order for a reagent to be a primary standard, it must be obtainable in pure form (generally at least 99.98% pure), stable both is pure form and in solution, easy to dry and keep dry, and soluble in a suitable solvent.

iii) But many useful reagents do not meet those requirements, so the reagent is dissolved and diluted approximately to the concentration desired. The solution is then standardised by titrating it against a primary solution. This standardised solution is called a secondary standard.

Requirements of a primary standard substance:

- It must be 100% pure and dry.
- It must be 100% soluble in suitable solvent.
- It should not be hygroscopic.
- It should get oxidized by oxygen or affected by CO_2
- The reactions should be stoichiometric and instantaneous.

1.5 Titration & Indicators: Titration is a widely used quantitative analytical technique. The steps involved in titration are as follows:

i) Prepare a solution from an accurately weighed sample to +/- 0.0001 g of the material to be analysed. It is also known as **Analyte**.

ii) Choose a substance that will react rapidly and completely with the analyte and prepare a standard solution of this substance. The concentration of the standard solution should be +/-0.0001 M. It is also known as **Titrant**.

iii) Place the standard solution in a burette and add it slowly to the solution of unknown concentration. This process is called **titration.** Continue the titration until the reaction is complete; that is, until the amount of reactant added is exactly the amount required to react with all the constituent being analysed. This point is called the **equivalence point**, and can be detected by adding an **indicator** to the unknown solution before beginning the titration.

iv) **An indicator** is a substance that gives a visible sign, usually by a colour change, of the presence or absence of a threshold concentration of a chemical species, such as an acid or an alkali in a solution. The point at which the colour change occurs is the end point of titration. An example of indicator is methyl yellow, which imparts a yellow colour to an alkaline solution. If acid is slowly added, the solution remains yellow until all the alkali has been neutralized, whereupon the colour suddenly changes to red. Indicators are classified as acid-base, oxidation-reduction, or specific-substance indicators, every indicator in each class having a characteristic transition range. Some of the commonly used acid-base indicators can be seen in Fig.2.

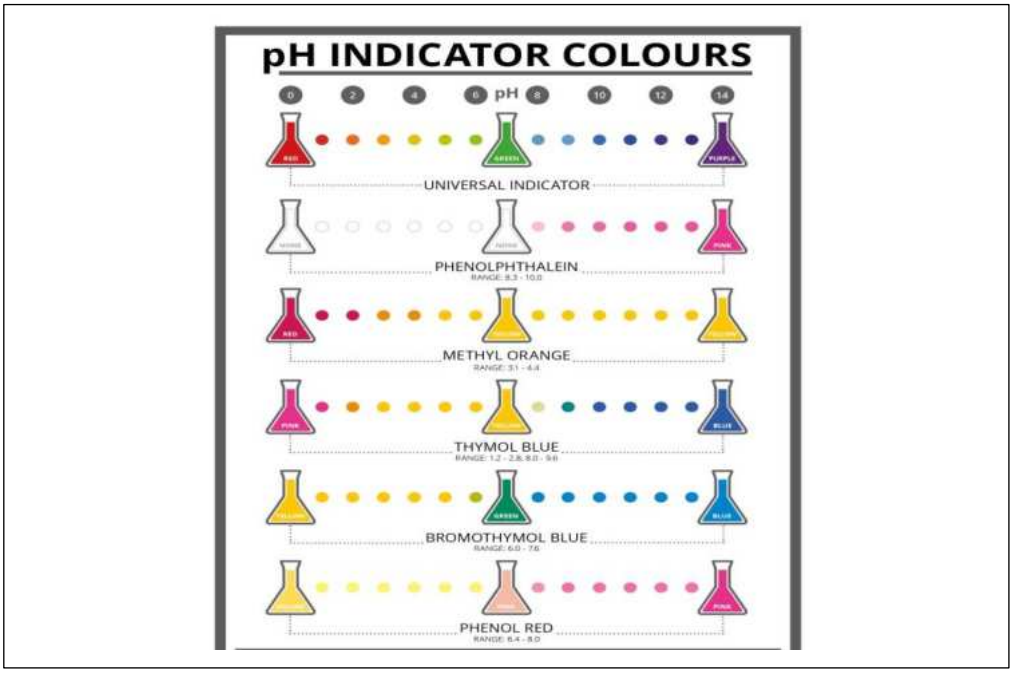

Fig.2. Some common pH indicators (Image courtesy: Compoundchem)

v) Measure the exact volume of standard solution required from burette readings before and after the titration. Since the molarity of the standard solution is known, the number of moles of titrant can be calculated. From a knowledge of the equation for the reaction, the number of moles of constituent present in sample can also be calculated.

1.6 Dilute solutions:

a) Dilution is the process of adding additional solvent to a solution to reduce its concentration. This process keeps the amount of solute constant, but increases the total amount of solution, thereby decreasing its final concentration. Dilution can be done by mixing a solution of higher concentration with an identical solution of lesser concentration. Diluting solutions is a routine process in the laboratory, as stock solutions are often purchased and stored in very concentrated forms. For the solutions to be usable in the lab (for a titration, for instance), they must be accurately diluted to a known, lesser concentration.

b) The volume of solvent needed to prepare the desired concentration of a new, diluted solution can be calculated mathematically. The relationship is as follows:

$M_1V_1 = M_2V_2$

Where

M_1 denotes the concentration of the original solution, and V_1 denotes the volume of the original solution; M_2 represents the concentration of the diluted solution, and V_2 represents the final volume of the diluted solution. When calculating dilution factors, it is important that the units for both volume and concentration are the same for both sides of the equation.

Example:

- 200 ml of a 1.6 M aqueous solution of NaCl is diluted with water to a final volume of 1.0 L. What is the final concentration of the diluted solution?

- $M_1V_1 = M_2V_2$
- (1.6 M) (200 ml) = M_2(1000 ml)
- M_2 = 0.32 M

c) Dilutions can sometimes be visually observed.

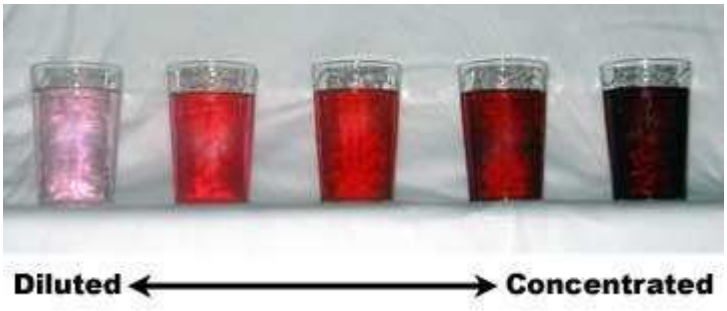

Fig.3. Intense red colour slowly fades as the solutions become more diluted

(Image courtesy*:* Lumen: Introduction to Chemistry)

c**) Serial dilutions:**

Serial dilutions involve diluting a stock or standard solution multiple times in a row. Typically, the dilution factor remains constant for each dilution, resulting in an exponential decrease in concentration. As for example, a ten-fold serial dilution could result in the following concentrations: 1 M, 0.1 M, 0.01 M, 0.001 M, and so on. As seen in this example, the concentration is reduced by a factor of ten in each step.

d) Serial dilutions are used to accurately create extremely diluted solutions, as well as solutions for experiments that require a concentration curve with an exponential or logarithmic scale. Serial dilutions are widely used in experimental sciences, including biochemistry, pharmacology, microbiology, and physics.

1.7 Units of concentration:

a) Most commonly, a solution's concentration is expressed in terms of normality, molarity, molality, formality etc.

b) **Normal solution:** A normal solution contains one gram equivalent mass of the substance in one liter of solution.

$$\text{Normality} = \frac{\text{Mass of the substance in one liter}}{\text{Gram equivalent mass of the substance}}$$

Example: 1.0 N HCl solution contains 36.45 gm of HCl in one litre of d/w

c) **Molarity:** It is a unit of concentration measuring the numbers of moles of a solute per litre of solution. Molarity is denoted with 'M'. A 1 M solution contains 1 mole of solute per litre of solution.

Example: 1.0 M HCl consists of 36.5gm HCl in 1000ml of distilled water

d) Molality: It is the number of moles of solute per kilogram of solvent. Solutions expressed in molal concentration are denoted with 'm'. 1 m solution contains 1 mole of solute per kilogram of solvent.

Example: 1.0 m H_2SO_4 solution contains 98gm of H_2SO_4 in 1000ml of water

e) Formality: It is defined as the number of formula mass of any solute dissolved in one litre of solution. A solution is said to be one formal (1 F) if it contains one formula mass of the substance in one litre of solution.

Example: 1.0 F solution of Oxalic acid ($H_2C_2O_4$, $2H_2O$) contains 126gm. Oxalic acid in one liter of solutions

1.8 Standard Curve: A standard curve also known as Calibration curve, is a type of graph used as a quantitative research technique. Standard curves represent the relationship between two quantities. Multiple samples with known concentration are measured and plotted on the graph, which then allows similar concentrations to be determined for unknown samples by interpolation on the graph. The samples with known concentration are the standards, and the graph is the standard graph.

Example: A standard curve for protein concentration determination.

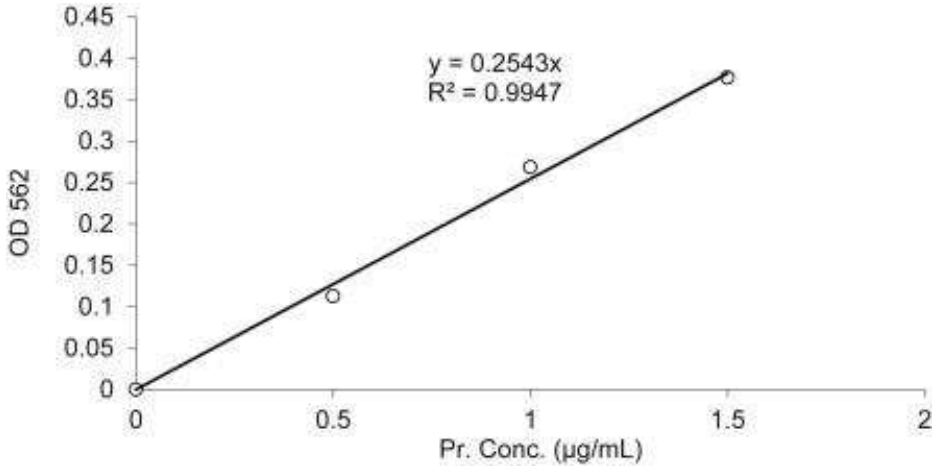

Fig.4. Standard curve example showing protein concentration determination

To calculate the sample concentration based on the standard curve, first we have to find out the concentration (on X-axis) for each sample absorbance (Optical density on Y -axis) using a spectrophotometer on the standard curve; then we have to multiply the concentration by the dilution factor for each sample.

1.9 Nomograph: Nomographs (or nomograms or alignment charts) are graphical representations of mathematical relationships which are used by simply applying a straight edge across the plot through the points on scales representing independent variables, which then crosses the corresponding datum point for the dependent variable; the choice among independent and dependent variable is arbitrary so that each variable may be determined in terms of the others. Common example of nomograms are:

use to compute the lift available for a hot-air balloon, the boiling points of solvents under reduced pressure and the relative forces in a centrifuge. Nomograms provide insight into mathematical relationships, are useful for rapid and repeated application, even in the absence of calculational facilities, and can reliably be used in the field.

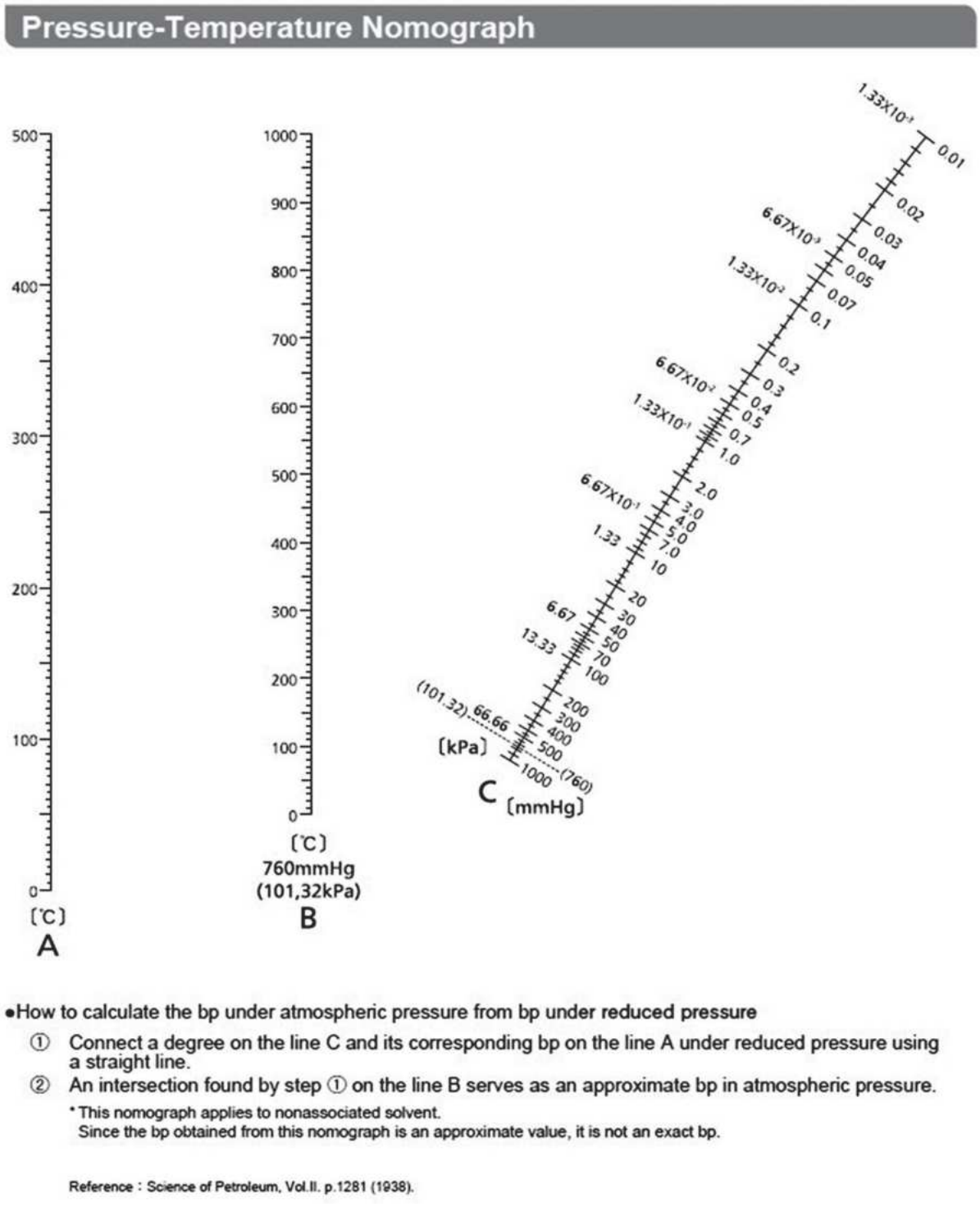

Fig.5. A Pressure-Temperature nomograph

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Lesson 2	Chemistry of water
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University/College Name	Sri Venkateswara Veterinary University,Tirupati

Lesson 2

Objectives:

1. To understand the structure, properties & composition of water

Glossary of terms:

Hydrogen Bond: There is an electrostatic attraction between the oxygen atom of one water molecule and hydrogen of another water molecule which is known as hydrogen bond.

Hydrophilic: Compounds that readily dissolves in water are referred to as Hydrophilic (Greek, "Water-loving").

Hydrophobic: Compounds that do not readily dissolve in water are termed as Hydrophobic.

Amphipathic compounds: Compounds that contain regions that are polar (or charged) and regions that are nonpolar.

Specific Heat: The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius.

Vapourisation: It is a process in which thermal energy make the water molecules loose from the liquid surface and into the gaseous state

Latent Heat of Vapourisation: This is the heat that required for vaporizing 1.0 gm. of water at 100^0C (540 Cal/gm).

Latent Heat of Fusion: The amount of heat required to change water from a solid state to a liquid state with no change in temperature is termed the latent heat of fusion.

Viscosity: It is a measurement of internal molecular friction of a liquid.

Adhesion: It is the tendency to cling to the surface of materials by means of hydrogen bonds of water molecule and oxygen atoms of the other substances.

Cohesion: Cohesion is the property of liquids which offers resistance to being pulled apart or to the formation of new surfaces.

Surface Tension: At the surface of a water mass, the force responsible for resistance is termed Surface Tension.

E-lecture:

1. The Water Molecule: A molecule of water is formed by bonding of two atoms of hydrogen (H) with one atom of oxygen (O) at an angle of 104.5^0. Each hydrogen atom of a water molecule shares an electron pair with the central oxygen atom. The geometry of the molecule is dictated by the shapes of the outer electron orbitals of the oxygen atom. The orbitals form a rough tetrahedron, with a hydrogen atom at each of the two corners and unshared electron pairs at the other two corners as seen in Fig. 1 (a,b). The H-O-H bond angle is 104.5^0 which is < than 109.5^0 of a perfect tetrahedron because of crowding by the nonbonding orbitals of the oxygen atom.

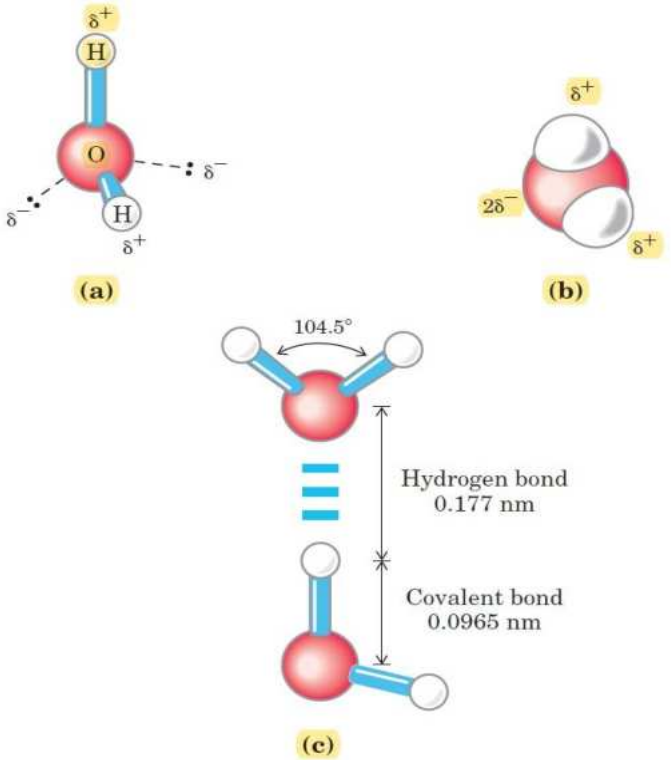


Fig. 1 Structure of the water molecule. The dipolar nature of the H_2O molecule is shown by (a) ball-and-stick and (b) space-filling models. The dashed lines in (a) represent the nonbonding orbitals. There is nearly a tetrahedral arrangement of the outer-shell electron pairs around the oxygen atom; the two hydrogen atoms have localised partial +ve charges (δ^+) and the oxygen atom has a partial negative charge ($2\delta^-$). (c) The H_2O molecules joined by a hydrogen bond (by three blue lines) between the oxygen atom of the upper molecule and a hydrogen atom of the lower one. Hydrogen bonds are longer and weaker than covalent OOH bonds. (Source: Principles of Biochemistry (2008, W.H.Freeman))

A) Hydrogen Bond: The oxygen nucleus attracts electrons more strongly than does the hydrogen nucleus (a proton); that is, oxygen is more electronegative. The sharing of electrons between H and O is therefore unequal; the electrons are more often in the vicinity of the oxygen atom than of the hydrogen. The result of this unequal electron sharing is two electric dipoles in the water molecule, one along each of the HOO bonds; each hydrogen bears a partial positive charge (δ^+) and the oxygen atom bears a partial negative charge equal to the sum of the two partial positives ($2\delta^-$). As a result, there is an electrostatic attraction between the oxygen atom of one water molecule and hydrogen of another as seen in Fig.1(c), called a hydrogen bond.

B) Hydrogen Bonding gives water its unusual properties: Water has a higher melting point, boiling point, and heat of vaporization than most other common solvents (Table 1). These unusual properties are mainly due to attractions between adjacent water molecules that give liquid water great internal cohesion.

Table.1 Melting point, Boiling point, and Heat of Vapourisation of some common solvents

Solvents	Melting point (^{0}C)	Boiling point (^{0}C)	Heat of Vapourisation ((J/g)
Water	0	100	2260
Methanol (CH_3OH)	-98	65	1100
Ethanol (CH_3CH_2OH)	-117	78	854
Propanol ($CH_3CH_2CH_2OH$	-127	97	687
Butanol ($CH_3(CH_2)_2CH_2OH$)	-90	117	590
Acetone (CH_3COCH_3)	-95	56	523
Hexane ($CH_3(CH_2)_4CH_3$)	-98	69	423
Benzene (C_6H_6)	6	80	394
Butane ($CH_3(CH_2)_2CH_3$)	-135	-0.5	381
Chloroform ($CHCl_3$)	-63	61	247

Hydrogen bonds are relatively weak. Those in liquid water have a bond dissociation energy (the energy required to break a bond) of about 23 kJ/mol, compared with 470 kJ/mol for the covalent OOH bond in water or 348 kJ/mol for a covalent COC bond. The hydrogen bond is about 10% covalent, due to overlaps in the bonding orbitals, and about 90% electrostatic.

C) At room temperature, the thermal energy of an aqueous solution (the kinetic energy of motion of the individual atoms and molecules) is of the same order of magnitude as that required to break hydrogen bonds. When water is heated, the increase in temperature reflects the faster motion of individual water molecules. At any given time, most of the molecules in

liquid water are engaged in hydrogen bonding, but the lifetime of each hydrogen bond is just 1 to 20 picoseconds (1 ps = 10^{-12} s), upon breakage of one hydrogen bond, another hydrogen bond
forms, with the same partner or a new one, within 0.1 ps. The sum of all the hydrogen bonds between H_2O molecules confers great internal cohesion on liquid water. Extended networks of hydrogen-bonded water molecules also form bridges between solutes (proteins and nucleic acids, for example) that allow the larger molecules to interact with each other over distances of several nanometers without physically touching.

D) The nearly tetrahedral arrangement of the orbitals about the oxygen atom (Fig. 1 a) allows each water molecule to form hydrogen bonds with as many as four neighboring water molecules. In liquid water at room temperature and atmospheric pressure, however, water molecules are disorganized and in continuous motion, so that each molecule forms hydrogen bonds with an average of only 3.4 other molecules. In ice, on the other hand, each water molecule is fixed in space and forms hydrogen bonds with a full complement of four other water molecules to yield a regular lattice structure (Fig. 2). Breaking a sufficient proportion of hydrogen bonds to destabilize the crystal lattice of ice requires much thermal energy, which accounts for the relatively high melting point of water (Table.1). When ice melts or water evaporates, heat is taken up by the system:

H_2O (Solid) ⟶ H_2O (Liquid) ⟶ H_2O (Gas) ΔH_{vap} = 44.0 kJ/mol

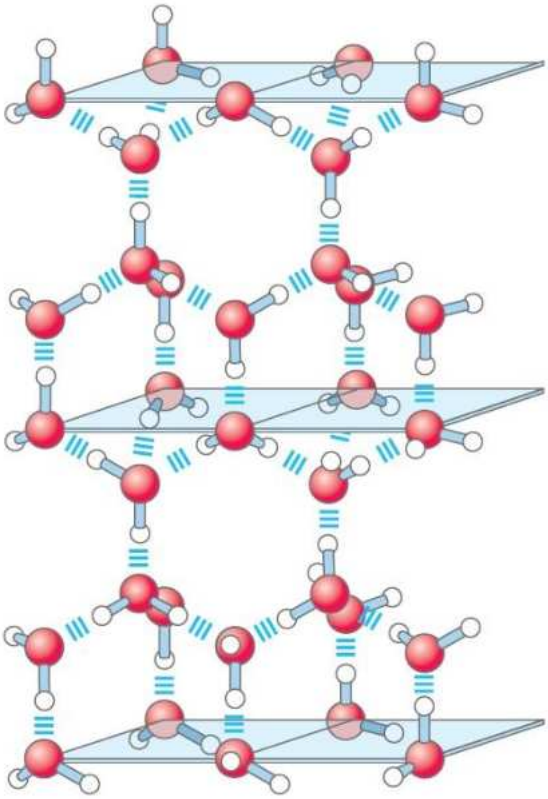


Fig.2 Hydrogen bonding in ice. In ice, each water molecule forms the maximum of four hydrogen bonds, creating a regular crystal lattice. By contrast, in liquid water at room temperature and atmospheric pressure, each water molecule hydrogen-bonds with an average of 3.4 other water molecules. This crystal lattice of ice makes it less dense than liquid water, and thus ice floats on liquid water. (Source: Principles of Biochemistry (2008, W.H.Freeman))

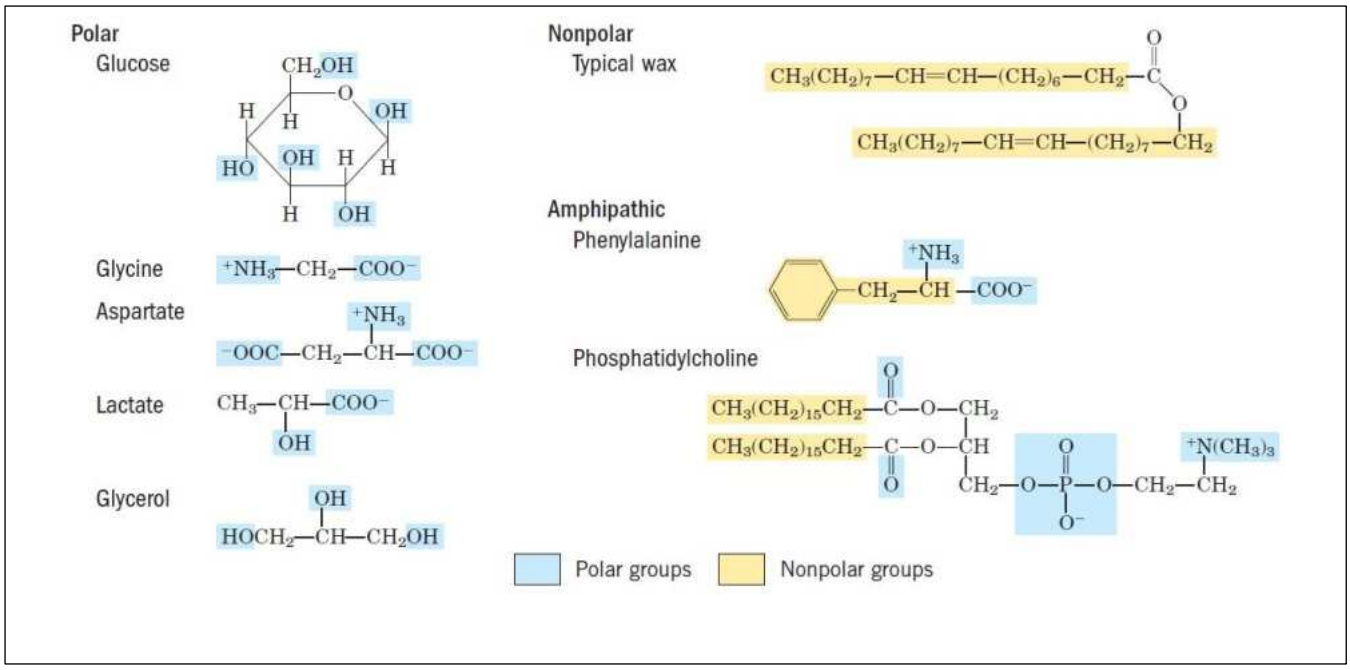
E) During melting or evaporation, the entropy of the aqueous system increases as more highly ordered arrays of water molecules relax into the less orderly hydrogen bonded arrays in liquid water or the wholly disordered gaseous state. At room temperature, both the melting of ice and the evaporation of water occur spontaneously; the tendency of the water molecules to associate through hydrogen bonds is outweighed by the energetic push toward randomness.

F) The water molecule is electrically polar in nature. This is because in the molecular structure of water, both hydrogen atoms are located on the

same side rather than being at opposite ends. This means that water molecule is not symmetrical but rather small boomeranged shape. One side of the molecule carries a net negative charge and the other side a net positive charge. This, the molecule is strongly electrically polarized. Water molecule is said to be a permanent dipole, containing a pair of equal and opposite electric charges. High dipolic movement of the water molecule makes water an excellent solvent for ionic compounds.

G) Water readily dissolves most biomolecules, which are generally charged or polar compounds (Table 2); compounds that dissolve easily in water are hydrophilic (Greek, "water-loving"). In contrast, nonpolar solvents such as chloroform and benzene are poor solvents for polar biomolecules but easily dissolve those that are hydrophobic—nonpolar molecules such as lipids and waxes.

Table. 2 Some examples of Polar, Nonpolar and Amphipathic Biomolecules (Shown as Ionic Forms at pH 7) (Source: Principles of Biochemistry (2008, W.H.Freeman))



2. Physical Properties of Water: Table 3 shows some of the basic physical properties of water. Some of these properties are affected by temperature; hence shown at different temperatures. Effect of these properties on water behaviour is also highlighted (Chang, 2010; Ebbing and Gammon, 2009; Manahan, 2000; Venkateswariu, 2003).

Table 3 Physical properties of water

Property	**Value**	**Temperature (^{0}C)**	**Effect & Significance**
Specific heat	1 cal		Water can absorb substantial amount of heat while its temperature rises only slightly.
Density	0.9999	0	Solid form is less dense than its liquid form; ice floats at the surface of liquid water
	1.000 g/mL	3.98	
	0.9971 g/mL	25	
	0.9584	100	
Viscosity	1.79 cP	0	Hot molasses flows much faster than cold molasses
	0.89 cP	25	
	0.28 cP	100	
Surface tension	75.6 dyn/cm	0	Water bugs (striders) seem to skitter
	72.5 dyn/cm	25	
	58.9 dyn/cm	100	

			across this skin as if ice-skating. You can actually float a pin on water, if you carefully lay it across the surface
Dipole moment	1.8546 D		Reflects the polarity of water molecule
Latent heat of fusion	80 cal	0	
Latent heat of vapourisation	540 cal	100	
Boiling point	100^0C (372K) at 1 atm		
Melting point	0^0C (273.2 K)		

2.1 Specific heat: The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius. Unit of specific heat is "Calorie". The calorie is defined as the amount of heat required to raise the temperature of one gram of water by one degree celecius (4.1868 Joule). Water has to absorb 4.184 Joules of heat for the temperature of one gram of water to increase 1 degree celsius (°C). For comparison sake, it only takes 0.385 Joules of heat to raise 1 gram of copper 1°C. Specific heat of water is 1 Cal. In natural waters dissolved substances lower the specific heat.

2.2 Latent Heat of vaporization (LHV): Vaporization is a process in which thermal energy make the water molecules loose from the liquid surface and into the gaseous state. Water has an exceptionally high latent heat of

vaporization. LHV is the heat that required vaporizing 1.0 gm. of water at 100^0C (540 Cal/gm).

2.3 Latent Heat of fusion: The amount of heat required to change water from a solid state to a liquid state with no change in temperature is termed the latent heat of fusion. 80 calories of heat is required to melt 1g of ice at 0^0C.

2.4 Density of water: Water becomes less dense at high temperature and denser at low temperature. Fresh water reaches its maximum density at the freezing point of water i.e. 3.98 ^{0}C. As it cools below 4^0C, the density decreases i.e. water becomes lighter due to formation of crystalline structure. Density is a function of temperature, pressure and concentration of dissolved or suspended substances.

2.5 Viscosity: It is the measurement of the internal molecular friction of a liquid. Viscosity is concerned with mobility and flow of water. Viscosity of water decreases with increasing temperature.

2.6 Adhesion: Adhesion is the tendency to cling to the surface of materials by means of hydrogen bonds of water molecule and oxygen atoms of the other substances.

2.7 Cohesion: Cohesion is the property of liquids which offers resistance to being pulled apart or to the formation of new surfaces.

2.8 Surface tension: At the surface of a water mass, the force responsible for resistance is termed as Surface Tension. Results from the unsymmetrical activity of water molecules on or below the surface (Fig.3). Surface tension could be defined as the property of the surface of a liquid that allows it to resist an external force, due to the cohesive nature of the water molecules. The surface tension of water is 72.5 dynes/cm at 25°C. It would take a force of 72.5 dynes to break a surface film of water 1 cm long. The surface tension of water decreases significantly with temperature. Species associated with the surface film are known as neuston.

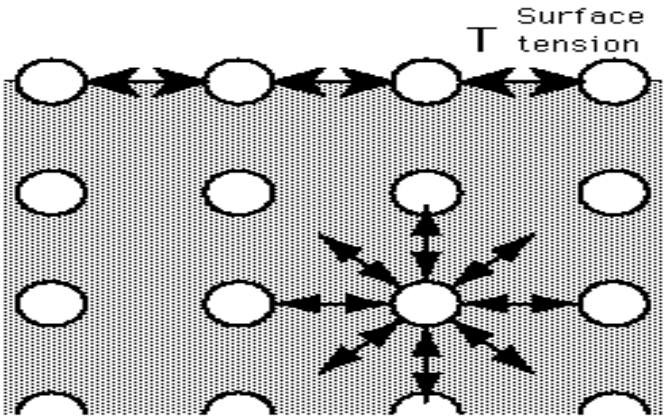


Fig.3 Surface tension of a water mass

3. Chemical properties of water: There are mainly 3 types of chemical reactions that could take place in water: Precipitation, Acid/base, and oxidation-reduction reaction.

- ✓ **Precipitation reaction:** dissolved ions react with each other and form a solid compound or precipitate. A typical precipitation reaction that occurs in water is the formation of calcium carbonate solid when solution of calcium is mixed with solution of carbonate (Davis and Cornwell, 2012).

$$Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow CaCO_{3(s)}$$

- ✓ **Neutralisation reaction:** A neutralization reaction is a reaction of an acid and a base that results in an ionic compound and possibly water. When a base is added to an acid solution, the acid is said to be neutralized. The ionic compound that is produced in a neutralization reaction is called a salt (Chang, 2010; Ebbing and Gammon, 2009). The net equation for most acid base reaction is:

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

- ✓ **Oxidation-reduction reaction:** It is a reaction in which electrons are transferred between species or in which atoms change oxidation number. The substance that loses the electron is said to be oxidized

and it is called a reducing agent. While the substance that accept the electron is said to be reduced and is called oxidizing agent. When one species release electron, another one should be available to accept the electron. Iron pipe corrosion is an example of oxidation–reduction reaction in which iron metal oxidizes and loses two electrons, while hydrogen ions accepts those electrons and reduces to hydrogen gas (Chang, 2010; Davis and Cornwell, 2012; Ebbing and Gammon, 2009)

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$2H^+ + 2e^- \longrightarrow H_{2\,(g)}$$

3.1 pH: The pH of a solution is a measure of hydronium ion (H_3O^+) concentration, which is, in turn, a measure of acidity. In acidic solutions the pH is less than 7, while it is greater than 7 in basic solutions. The pH range in water samples is rarely below 4 or above 10. Determining pH of water is essential as it affects many of the chemical and biological processes that take place in water (Davis and Cornwell, 2012; Venkateswariu, 2003).

3.2 Alkalinity: Alkalinity refers to as buffering capacity of water to neutralise water. It is defined as the sum total of all titratable bases down to about pH 4.5. It is found experimentally by determining how much acid it takes to lower the pH of water to 4. The alkalinity of water is mainly contributed by bicarbonate, carbonate and hydroxide ions.

3.3 Water Hardness: Hardness is the sum total of all polyvalent cations. Practically it is the sum of calcium and magnesium ions which are predominant cations in natural waters. Hardness is expressed in mg/L as $CaCO_3$, as in alkalinity. Both calcium and magnesium have a valence of two when converting to $CaCO_3$. The sum of calcium and magnesium is the total hardness (TH), which is subdivided to carbonate and noncarbonated hardness.

Carbonate hardness is often called temporary hardness because heating the water will remove it. When water is heated, the insoluble carbonates precipitate and tend to form bottom deposits in hot water heaters. Carbonate hardness is equal to the total hardness or alkalinity, whichever is less.

Noncarbonated hardness is correspondingly called permanent hardness because it is not removed when water is heated. Noncarbonated hardness is the total hardness in excess of the alkalinity. If the alkalinity is equal to or greater than the total hardness, there is no noncarbonated hardness (Davis and Cornwell, 2012; Manahan, 2000).

3.4 Sea Water: Chemical analyses of samples from all over the world show that seawater consists of a small quantity of salt dissolved in water. The salt occurs as charged particles, cations and anions, that are dispersed among the molecules of liquid water. Seawater is a chemical solution. The dissolving agent, the liquid water, is the solvent and the dissolved substances, the salt ions, are the solute. Seawater also contains minor to trace amounts of dissolved metals, nutrients, gases, and organic compounds of seemingly infinite variety.

A) Salinity: Average or "normal" seawater has a salinity of about 35‰. This means that the dissolved salt occurs in a concentration of 35 parts per thousand (ppt). That is, the salt comprises 3.5 percent (divide 35 by 1,000, and convert it to a percentage by multiplying it by 100) of the sample, the rest (96.5 percent or 965 parts per thousand) being H_2O molecules.

B) Major constituents: In terms of quantity, the primary solutes in seawater are cations and anions. By weight, chloride (Cl^-) and sodium (Na^+) together comprise more than 85.65 percent (Table 4) of all the dissolved substances in seawater. When these two ions bond chemically into a solid, they form halite and give seawater its most distinctive property—its saltiness. The six most abundant ions—chloride (Cl^-), sodium (Na^+), sulfate ($SO4^{2-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+)—make up over 99 percent of all of seawater's solutes. The addition of five more

solutes to the list—bicarbonate (HCO^{3-}), bromide (Br^{-}), boric acid (H_3BO_3), strontium (Sr^{2+}), and fluoride (F^{-})—elevates the quantity of dissolved ingredients in seawater to 99.99 percent.

Table 4 Major solutes in Seawater

Salt Ion	**Ions in Seawater* (%)**	**Ions by Weight (%)**	**Cumulative (%)**
Chloride (Cl^{-})	18.980	55.04	55.04
Sodium (Na^{+})	10.556	30.61	85.65
Sulfate (SO_4^{2-})	2.649	7.68	93.33
Magnesium (Mg^{2+})	1.272	3.69	97.02
Calcium (Ca^{2+})	0.400	1.16	98.18
Potassium (K^{+})	0.380	1.10	99.28
Bicarbonate (HCO_3^{-})	0.140	0.41	99.69
Bromide (Br^{-})	0.065	0.19	99.88
Boric acid (H_3BO_3)	0.026	0.07	99.95
Strontium (Sr^{2+})	0.013	0.04	99.99
Fluoride (F^{-})	0.001	0.00	99.99
Total	**34.482**	**99.99**	**99.99**

*The gram weight of ions per 1 kg of seawater, or g/kg.

Source: Adapted from Sverdrup, H. U., Johnson, M. W., and Fleming, R. H. *The Oceans* (Englewood Cliffs, N.J.: Prentice-Hall, 1942).

C) Nutrients: Nutrients in seawater are compounds that consist primarily of nitrogen (N), phosphorous (P), and silicon (Si). Representative concentrations of these nutrients in the ocean are listed in Table 5.

Table 5 Near surface nutrient concentration in seawater

Nutrient element	Concentration (ppm)
Phosphorus (P)	0.07
Nitrogen (N)	0.5
Silicon (Si)	3

D) Gases: 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) (Table 6). Nitrogen and the three noble gases are inert (unreactive) and rarely involved 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 nonconservative.

Table 6 Quantities of Gas in Air & Seawater

Gas	In Dry Air (%)	In Surface Ocean Water (%)	Water-Air ratio
Nitrogen (N_2)	78.03	47.5	0.6
Oxygen (O_2)	20.99	36.0	1.7
Carbon dioxide (CO_2)	0.03	15.1	503.3
Argon (Ar), hydrogen (H_2), neon (Ne), and helium (He)	0.95	1.4	1.5

E) Trace elements: Most trace elements, such as manganese (Mn), lead (Pb), mercury (Hg), gold (Au), iodine (I), and iron (Fe), occur in concentrations of less than 1 ppm (part per million) (Table 7). 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, either by helping to promote life or by retarding or killing life (toxicity).

Table 7 Trace elements in Seawater

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

F) Organic compounds: Organic compounds are large, complex molecules produced by organisms. They include substances such as lipids (fats), proteins, carbohydrates, hormones, and vitamins. Typically, they occur in low concentrations and are produced by metabolic (physical and chemical processes in the cell of an organism that produce living matter) and decay processes of organisms.

4.Composition of Waters: In earth crust and atmosphere, water is available in different forms as shown in Table 7.

Table 8 Forms of water in earth's crust and atmosphere

Forms of Water	Percentage (%)
Salt water	97.20%
Freshwater	2.80%
Ice	2.00%
Groundwater	0.62%
Freely available water	0.18 %
Moisture	0.001%

Chemical analysis of water samples from rivers all over the world indicate that they contain a variety of dissolved substances (Table 9). The source of these substances is chemical weathering of rocks on the land. These rocks are made up of an assemblage of minerals composed predominantly of the elements silicon, aluminium, and oxygen. Acidic waters breaks down these rocks into their component elements.

Table 9 Dissolved substances in River water

Substance	Concentration (ppm)	Concentration (%)
Bicarbonate/carbonate (HCO_3^-/CO_3^{2-})	58.8	48.7
Calcium (Ca^{2+})	15.0	12.4
Silica (SiO_2)	13.1	10.8
Sulfate (SO_4^{2-})	1.2	9.3
Chloride (Cl^-)	7.8	6.5
Sodium (Na^+)	6.3	5.2
Magnesium (Mg^{2+})	4.1	3.4
Potassium (K^+)	2.3	1.9
Nitrate (NO_3^-)	1.0	0.8
Iron aluminum oxide [$(Fe, Al)_2 O_3$]	0.9	0.8
Remainder	0.3	0.3

Source: Livingstone, D. A. Chemical composition of rivers and lakes, U.S. Geological Survey, Professional Paper 440-G (U.S. Government Printing Office, 1963).

4.1 Chemistry of Surface Water: Surface water is extremely variable in its chemical composition depending upon the interaction with the rocks on which it flows and in relative contribution of ground water and surface water run-off. The mineral content in river water usually bears an inverse relationship to discharge. The mineral content of river water tends to increase from source to mouth, although the increase may not be continuous or uniform. Other factors like discharge of wastewater from the cities located on the banks, industrial waste etc can also affect the nature and concentration of various chemical constituents in surface water. Among anions, HCO_3 is most important (>50% of the total anions in meq/L). In case of cations, the alkaline earth, viz, Ca predominates. With increasing salinity the hydrochemical facies tends to change from Ca-HCO_3 to mixed cation to Na-HCO_3 and finally to Na-Cl type.

4.2 Chemistry of Ground Water:

a) The quality of ground water is generally considered to be superior to surface water because of the purifying effects of the soil column and vadose zone during the process of percolation. The final composition of groundwater depends on the mineralogic composition of the aquifer framework and contact time or age of the water. According to Mathess (1982), the processes affecting the quality are dissolution, hydrolysis, precipitation, adsorption, ionexchange, oxidation, reduction and bio-chemical mediated reactions. In general, the reactions that control the chemistry of ground water are:

- Introduction of CO_2 gas into the unsaturated zone.
- Dissolution of calcite and dolomite and precipitation of calcite.
- Cation-exchange.
- Oxidation of pyrite and organic matter.

- Reduction of oxygen, nitrate and sulphate with production of sulphide.
- Reductive production of methane.
- Dissolution of gypsum, anhydrite and halite.
- Incongruent dissolution of primary silicates with formation of clays.

b) Ground water that is in perpetual motion, acquires various physical, chemical and biological characteristics as it flows from recharge area to the discharge area. The factors that influence ground water quality are:

- Local geology,
- Land use,
- Climatic conditions particularly pattern and frequency of rainfall
- Anthropogenic activities such as use of fertilizers and pesticides in agriculture,
- Disposal of domestic sewage and industrial effluents and
- Extent of exploitation of ground water resources.

c) The oxygen present in water is used for the oxidation of organic matter that subsequently generates CO_2 to form H_2CO_3. This process goes on until oxygen is fully consumed.

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

d) In addition to these, there are several other basic reactions involving microbiological mediated reactions, which tend to alter the chemical composition of the percolating waters. Percolating water is charged with oxygen and carbon dioxide and is most aggressive in the first part. This water gradually loses its aggressiveness, as free CO_2 associated with the percolating water gets gradually exhausted through interaction of water with minerals.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

$$H^+ + \text{Feldspar} + H_2O \longrightarrow \text{Clay} + H_4SiO_4 + \text{Cation}$$

Some rocks serve as sources of chloride and sulphate through direct solution. The circulation of sulphur, however, may be greatly influenced by biologically mediated oxidation and reduction reactions. Chloride circulation may be a significant factor influencing the anion content in many natural waters.

The list of the chemical constituents present in groundwater in varying proportions are shown in Table 1 (Todd, 1999)

Table 10: Major, Minor & Trace constituents of ground water

Constituent classes	**Constituents**
Major Constituents (1.0 to 1000 mg/L)	Sodium,Calcium,Magnesium,Bicarbonate,Sulfate,Chl oride,Silica
Secondary Constituents(0.01to10.0 mg/L)	Iron,Strontium,Potassium,Carbonate,Nitrate, Fluoride, Boron
Minor Constituents (0.0001 to 0.1 mg/L)	Antimony,Aluminium,Arsenic,Barium,Bromide,Cadmium,Chromium,Cobalt,CopperGermanium,Iodide,Lead,Lithium,Manganese,Molybdenum,Nickel,Phosphate,Rubidium,Selenium,Titanium,Uranium,Vanadium ,Zinc
Trace Constituents (generally less than 0.001 mg/L)	Beryllium,Bismuth,Cerium,Cesium,Gallium,Gold,Indium,Lanthanum,Niobium,Platinum,Radium, Ruthenium,Scandium,Silver,Thallium,Thorium,Tin,Tungsten ,Ytterbium, Yttrium, Zirconium

4.3 Dissolved gases:

a) Polar gases are generally more soluble in water compared to non-polar gases. The molecules of the biologically important gases CO_2, O_2, and N_2 are nonpolar. In O_2 and N_2, electrons are shared equally by both atoms. In CO_2, each C=O bond is polar, but the two dipoles are oppositely directed and cancel each other (Table 11). The movement of molecules from the disordered gas phase into aqueous solution constrains their motion and the motion of water molecules and therefore represents a decrease in entropy. The nonpolar nature of these gases and the decrease in entropy when they enter solution combine to make them very poorly soluble in water (Table 11). Gases like NH_3 and H_2S which are polar dissolve readily in water.

Table 11: Solubilities of some gases in water (Source: Principles of Biochemistry (2008, W.H.Freeman))

b) Gases present in water enters from the atmosphere; very rare gases come from radioactive decay processes with in the sediment in the ocean.

Course Name	Soil and Water Chemistry
Lesson 1	Analytical Chemistry: Principles, Applications and Ty
Course Revisor Name	Dr. Rajdeep Dutta
University/College Name	Assam Agricultural University, Jorhat
Course Reviewer Name	T V Ramana
University/College Name	Sri Venkateswara Veterinary University,Tirupati

Molarity: It is a unit of concentration measuring the numbers of moles of a solute per litre of solution. Molarity is denoted with 'M'. A 1 M solution contains 1 mole of solute per litre of solution.

Molality: It is the number of moles of solute per kilogram of solvent. Solutions expressed in molal concentration are denoted with 'm'. 1 m solution contains 1 mole of solute per kilogram of solvent.

Formality: It is defined as the number of formula mass of any solute dissolved in one litre of solution. A solution is said to be one formal (1 F) if it contains one formula mass of the substance in one litre of solution.

Standard curve: A standard curve also known as Calibration curve, is a type of graph used as a quantitative research technique. Multiple samples with known concentration are measured and plotted on the graph, which then allows similar concentrations to be determined for unknown samples by interpolation on the graph. The samples with known concentration are the standards, and the graph is the standard graph.

Nomograph: These are graphical representations which are used by simply applying a straight edge across the plot through the points on scales representing independent variables, which then crosses the corresponding datum point for the dependent variable; the choice among independent and dependent variable is arbitrary so that each variable may be determined in terms of the others.

E-lecture:

1. What is Analytical Chemistry: Analytical chemistry is application of chemical knowledge for characterising the composition of matter, both qualitatively and quantitatively (the identification of matter under study is performed using qualitative analysis while quantitative analysis is used to determine how much (relative concentration or total amount) of the substance is present in the analyte . Methods used in analytical chemistry

by finding its concentration based on the exact amount of corresponding base or acid required to neutralize it. Complexometric titration is a volumetric analysis where end point of titration is the formation of a characteristic coloured complex, which is usually a metal complex.

(b) Gravimetric methodIt uses precipitation or volatilization to determine the mass of the analyte from its ionic mass. Precipitation, Volatilization or electroanalytical methods are mostly used.

(c) Coulometric method:These methods help to determine the mass of matter transformed by electrolysis from the amount of electric current used or produced during the reaction.

1.2 Instrumental methods:Instrumental methods are mostly used in advance level of research and the same instrument may be used to separate, identify and quantify the analyte.

A) Instrumental separation methods:

(a) Chromatography:This method uses a mobile phase into which the mixture is introduced, which then passed through the stationary phase. Due to the different rates at which the components of the mixture travel through the stationary phase, they can be separated.

There are different types of chromatography:

(i) Paper or thin layer chromatography

(ii) Gas chromatography

(iii) Ion-exchange and size-exclusion chromatography

(iv) Reversed-phased chromatography, Two-dimensional chromatography, Hydrophobic interaction chromatography

Special Note

High Performance Liquid Chromatography (HPLC) is an advance technique which the analyte is contained in a mobile phase passed through a stainless-steel which is between 1 and 25 cm long and less than 1.0 mm to 4.6 mm internal dia filled tightly with micro size particles allowing the various components of a com non-volatile mixture to separate rapidly. The final concentration is determined computations based on the outputs at varying amounts of organic compound.

instruments. Irradiance is the intensity of light and is measured in watts per square meter.

1.3 Volumetry & Gravimetry:

A) Volumetry:It is a widely used quantitative analytical method. It involves measurement of volume of a solution of known concentration which is used to find out the concentration of the analyte.

Some of the widely used volumetric analysis are:

a) Acidimetry: The term acidimetry refers to that part of volumetric analysis whereby an acid solution at known concentration, along with a specific indicator, is used to titrate a base solution and thus work out its concentration.

b) Alkalimetry: The term alkalimetry refers to that part of volumetric chemical analysis which enables us to work out the concentration of an acid solution using an alkaline solution at a known concentration and a suitable indicator.

c) Argentometry: The determination of silver or halides by the precipitation of silver salts is known as argentometric titrations. The sample solution is titrated against a solution of silver nitrate of known concentration. It can be used for measurement of salinity.

B) Gravimetry:Gravimetric analysis is a technique through which the amount of an analyte (the ion being analysed) can be determined through the measurement of mass. Gravimetric analyses depend on comparing the masses of two compounds containing the analyte.

Principle:Mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

For an accurate gravimetric analysis, the following 3 conditions must be met:

i) The ion being analysed must be completely precipitated.

ii). The precipitate must be pure compound.

iii) The precipitate must be easily filtered.

1.4 Standard Solutions: A solution whose strength or concentration is accurately known is referred to as Standard solution.

i) The most accurate and convenient way of preparing a standard solution is to weigh the reagent, dissolve it, and dilute the solution to a definite volume in a volumetric flask. However, this method can only be used if the reagent is a primary standard.

ii) In order for a reagent to be a primary standard, it must be obtainable in pure form (generally at least 99.98% pure), stable both is pure form and in solution, easy to dry and keep dry, and soluble in a suitable solvent.

iii) But many useful reagents do not meet those requirements, so the reagent is dissolved and diluted approximately to the concentration desired. The solution is then standardised by titrating it against a primary solution. This standardised solution is called a secondary standard.

Requirements of a primary standard substance:

- It must be 100% pure and dry.
- It must be 100% soluble in suitable solvent.
- It should not be hygroscopic.
- It should get oxidized by oxygen or affected by CO_2
- The reactions should be stoichiometric and instantaneous.

1.5 Titration & Indicators: Titration is a widely used quantitative analytical technique. The steps involved in titration are as follows:

i) Prepare a solution from an accurately weighed sample to +/- 0.0001 g of the material to be analysed. It is also known as Analyte.

ii) Choose a substance that will react rapidly and completely with the analyte and prepare a standard solution of this substance. The concentration of the standard solution should be +/-0.0001 M. It is also known as Titrant.

1.7 Units of concentration:

a) D } • š } u u } v o Ç U • } o µ š] } v [• } v v š Œ š] } v] • Æ normality, molarity, molality, formality etc.

b) Normal solution: A normal solution contains one gram equivalent mass of the substance in one liter of solution.

$$\text{Normality} = \frac{\text{Mass of the substance in one liter}}{\text{Gram equivalent mass of the substance}}$$

Example: 1.0 N HCl solution contains 36.45 gm of HCl in one litre of d/w

c) Molarity: It is a unit of concentration measuring the numbers of moles of a solute per litre of solution. Molarity is denoted with 'M'. A 1 M solution contains 1 mole of solute per litre of solution.

Example: 1.0 M HCl consists of 36.5gm HCl in 1000ml of distilled water

d) Molality: It is the number of moles of solute per kilogram of solvent. Solutions expressed in molal concentration are denoted with 'm'. 1 m solution contains 1 mole of solute per kilogram of solvent.

Example: 1.0 m H_2SO_4 solution contains 98gm of H_2SO_4 in 1000ml of water

e) Formality: It is defined as the number of formula mass of any solute dissolved in one litre of solution. A solution is said to be one formal (1 F) if it contains one formula mass of the substance in one litre of solution.

Example: 1.0 F solution of Oxalic acid ($C_2H_2O_4$, $2H_2O$) contains 126gm. Oxalic acid in one liter of solutions

1.8 Standard Curve:A standard curve also known as Calibration curve, is a type of graph used as a quantitative research technique. Standard curves represent the relationship between two quantities. Multiple samples with known concentration are measured and plotted on the graph, which then allows similar concentrations to be determined for unknown samples by interpolation on the graph. The samples with known concentration are the standards, and the graph is the standard graph.

Example:A standard curve for protein concentration determination.

Fig.4. Standard curve example showing protein concentration determination

To calculate the sample concentration based on the standard curve, first we have to find out the concentration (on X-axis) for each sample absorbance (Optical density on Y -axis) using a spectrophotometer on the standard curve; then we have to multiply the concentration by the dilution factor for each sample.

1.9 Nomograph:Nomographs (or nomograms or alignment charts) are graphical representations of mathematical relationships which are used by simply applying a straight edge across the plot through the points on scales representing independent variables, which then crosses the corresponding datum point for the dependent variable; the choice among independent and dependent variable is arbitrary so that each variable may be determined in terms of the others. Common example of nomograms are:

use to compute the lift available for a hot-air balloon, the boiling points of solvents under reduced pressure and the relative forces in a centrifuge. Nomograms provide insight into mathematical relationships, are useful for rapid and repeated application, even in the absence of calculational facilities, and can reliably be used in the field.

Fig.5. A Pressure-Temperature nomograph

Fig.2 Hydrogen bonding in ice. In ice, each water molecule forms the maximum of four hydrogen bonds, creating a regular crystal lattice. By contrast, in liquid water at room temperature and atmospheric pressure, each water molecule hydrogen-bonds with an average of 3.4 other water molecules. This crystal lattice of ice makes it less dense than liquid water, and thus ice floats on liquid water(Source: Principles of Biochemistry (2008, W.H.Freeman))

E) During melting or evaporation, the entropy of the aqueous system increases as more highly ordered arrays of water molecules relax into the less orderly hydrogen bonded arrays in liquid water or the wholly disordered gaseous state. At room temperature, both the melting of ice and the evaporation of water occur spontaneously; the tendency of the water molecules to associate through hydrogen bonds is outweighed by the energetic push toward randomness.

F) The water molecule is electrically polar in nature. This is because in the molecular structure of water, both hydrogen atoms are located on the

same side rather than being at opposite ends. This means that water molecule is not symmetrical but rather small boomeranged shape. One side of the molecule carries a net negative charge and the other side a net positive charge. This, the molecule is strongly electrically polarized. Water molecule is said to be a permanent dipole, containing a pair of equal and opposite electric charges. High dipolic movement of the water molecule makes water an excellent solvent for ionic compounds.

G) Water readily dissolves most biomolecules, which are generally charged or polar compounds (Table 2); compounds that dissolve easily in water are Z Ç Œ } ‰ Z] o] ~ '-Œ} À]l P^_Á• Xš /Œ } v š Œ • š U v } v ‰ } o Œ chloroform and benzene are poor solvents for polar biomolecules but easily dissolve those that are hydrophobic nonpolar molecules such as lipids and waxes.

Table. 2 Some examples of Polar, Nonpolar and Amphipathic Biomolecules (Shown as Ionic Forms at pH (Source: Principles of Biochemistry (2008, W.H.Freeman))

Fig.3 Surface tension of a water mass

3. Chemical properties of water: There are mainly 3 types of chemical reactions that could take place in water: Precipitation, Acid/base, and oxidation-reduction reaction.

- Precipitation reaction: dissolved ions react with each other and form a solid compound or precipitate. A typical precipitation reaction that occurs in water is the formation of calcium carbonate solid when solution of calcium is mixed with solution of carbonate (Davis and Cornwell, 2012).

$$Ca^{2+}_{(aq)} + CO^{2-}_{3\,(aq)} \longrightarrow CaCO_{3(s)}$$

- Neutralisation reaction: A neutralization reaction is a reaction of an acid and a base that results in an ionic compound and possibly water. When a base is added to an acid solution, the acid is said to be neutralized. The ionic compound that is produced in a neutralization reaction is called a salt (Chang, 2010; Ebbing and Gammon, 2009). The net equation for most acid base reaction is:

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \longrightarrow H_2O_{(l)}$$

- Oxidation-reduction reaction: It is a reaction in which electrons are transferred between species or in which atoms change oxidation number. The substance that loses the electron is said to be oxidized

Table 5 Near surface nutrient concentration in seawater

Nutrient element	Concentration (ppm)
Phosphorus (P)	0.07
Nitrogen (N)	0.5
Silicon (Si)	3

D) Gases: 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) (Table 6). Nitrogen and the three noble gases are inert (unreactive) and rarely involved 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 nonconservative.

Table 6 Quantities of Gas in Air & Seawater

Gas	In Dry Air (%)	In Surface Ocean Water (%)	Water-Air ratio
Nitrogen (N_2)	78.03	47.5	0.6
Oxygen (O_2)	20.99	36.0	1.7
Carbon dioxide (CO_2)	0.03	15.1	503.3
Argon (Ar), hydrogen (H_2), neon (Ne), and helium (He)	0.95	1.4	1.5

E) Trace elements: Most trace elements, such as manganese (Mn), lead (Pb), mercury (Hg), gold (Au), iodine (I), and iron (Fe), occur in concentrations of less than 1 ppm (part per million) (Table 7). 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, either by helping to promote life or by retarding or killing life (toxicity).

Table 7 Trace elements in Seawater

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

F) Organic compounds:Organic compounds are large, complex molecules produced by organisms. They include substances such as lipids (fats), proteins, carbohydrates, hormones, and vitamins. Typically, they occur in low concentrations and are produced by metabolic (physical and chemical processes in the cell of an organism that produce living matter) and decay processes of organisms.

4.Composition of Waters:In earth crust and atmosphere, water is available in different forms as shown in Table 7.

Table 8 Forms of water in earth's crust and atmosphere

Forms of Water	Percentage (%)
Salt water	97.20%
Freshwater	2.80%
Ice	2.00%
Groundwater	0.62%
Freely available water	0.18 %
Moisture	0.001%

Chemical analysis of water samples from rivers all over the world indicate that they contain a variety of dissolved substances (Table 9). The source of these substances is chemical weathering of rocks on the land. These rocks are made up of an assemblage of minerals composed predominantly of the elements silicon, aluminium, and oxygen. Acidic waters breaks down these rocks into their component elements.

Table 9 Dissolved substances in River water

Substance	Concentration (ppm)	Concentration (%)
Bicarbonate/carbonate (HCO_3^-/CO_3^{2-})	58.8	48.7
Calcium (Ca^{2+})	15.0	12.4
Silica (SiO_2)	13.1	10.8
Sulfate (SO_4^{3-})	1.2	9.3
Chloride (Cl^-)	7.8	6.5
Sodium (Na^+)	6.3	5.2
Magnesium (Mg^{2+})	4.1	3.4
Potassium (K^+)	2.3	1.9
Nitrate (NO_3^-)	1.0	0.8
Iron aluminum oxide [$(Fe Al)_2 O_3$]	0.9	0.8
Remainder	0.3	0.3

- ¾ Reduction of oxygen, nitrate and sulphate with production of sulphide.
- ¾ Reductive production of methane.
- ¾ Dissolution of gypsum, anhydrite and halite.
- ¾ Incongruent dissolution of primary silicates with formation of clays.

b) Ground water that is in perpetual motion, acquires various physical, chemical and biological characteristics as it flows from recharge area to the discharge area. The factors that influence ground water quality are:

- ¾ Local geology,
- ¾ Land use,
- ¾ Climatic conditions particularly pattern and frequency of rainfall
- ¾ Anthropogenic activities such as use of fertilizers and pesticides in agriculture,
- ¾ Disposal of domestic sewage and industrial effluents and
- ¾ Extent of exploitation of ground water resources.

c) The oxygen present in water is used for the oxidation of organic matter that subsequently generates CO_2 to form H_2CO_3. This process goes on until oxygen is fully consumed.

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

d) In addition to these, there are several other basic reactions involving microbiological mediated reactions, which tend to alter the chemical composition of the percolating waters. Percolating water is charged with oxygen and carbon dioxide and is most aggressive in the first part. This water gradually loses its aggressiveness, as free CO_2 associated with the percolating water gets gradually exhausted through interaction of water with minerals.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$$

$$H^+ + \text{Feldspar} + H_2O \longrightarrow \text{Clay} + H_4SiO_4 + \text{Cation}$$

Some rocks serve as sources of chloride and sulphate through direct solution. The circulation of sulphur, however, may be greatly influenced by biologically mediated oxidation and reduction reactions. Chloride circulation may be a significant factor influencing the anion content in many natural waters.

The list of the chemical constituents present in groundwater in varying proportions are shown in Table 1 (Todd, 1999)

Table 10: Major, Minor & Trace constituents of ground water

Constituent classes	Constituents
Major Constituents (1.(to 1000 mg/L)	Sodium,Calcium,Magnesium,Bicarbonate, fate,Chl oride,Silica
Secondary Constituents(0.01to10.0 mg/L)	Iron,Strontium,Potassium,Carbonate,Nitrat Fluoride, Boron
Minor Constituents (0.0001 to 0.1 mg/L)	Antimony,Aluminium,Arsenic,Barium,Brom e,Cad mium,Chromium,Cobalt,CopperGermaniur odide,L ead,Lithium,Manganese,Molybdenum,Nick ,Phosph ate,Rubidium,Selenium,Titanium,Uranium, anadium ,Zinc
Trace Constituent (generally less than 0.0(mg/L)	Beryllium,Bismuth,Cerium,Cesium,Gallium old,In dium,Lanthanum,Niobium,Platinum,Radiur Rutheni um,Scandium,Silver,Thallium,Thorium,Tin, ngsten ,Ytterbium, Yttrium, Zirconium

4.3 Dissolved gases:

a) Polar gases are generally more soluble in water compared to non-polar gases. The molecules of the biologically important gases O_2, CO_2 and N_2 are nonpolar. In O_2 and N_2, electrons are shared equally by both atoms. In CO_2, each C=O bond is polar, but the two dipoles are oppositely directed and cancel each other (Table 11). The movement of molecules from the disordered gas phase into aqueous solution constrains their motion and the motion of water molecules and therefore represents a decrease in entropy. The nonpolar nature of these gases and the decrease in entropy when they enter solution combine to make them very poorly soluble in water (Table 11). Gases like NH_3 and H_2S which are polar dissolve readily in water.

Table 11: Solubilities of some gases in water (Source: Principles of Biochemistry (2008, W.H.Freeman))

b) Gases present in water enters from the atmosphere; very rare gases come from radioactive decay processes with in the sediment in the ocean.