NAME: Ibrahim Shalash

ID: UD53394SEN62351

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Introduction:

Water chemistry is the branch of chemistry that concerns about water and its constituents, Such as salts, suspended solids, gases, and organic matter. Water chemistry is considered as the keystone that connects the principles of chemistry and other environmental sciences like atmospheric science, hydrogeochemistry, oceanography, biogeochemistry, soil chemistry, marine chemistry, limnological chemistry,… etc.

The constituents of water and their exact concentrations are of great importance for the determination of water use. The increase or decrease in the concentration of any constituent in water is a matter of life or death for aquatic life, or it essential to determine the suitability of water for human beings. Also, the constituents determine the suitability of water for irrigation and cattle.

A water chemist and a water engineer must have great knowledge about the reactions that take place in water bodies between water constituents, and their effect on water quality, before construction of various water and wastewater treatment plants.

Water chemists have to know basic chemistry principles such as equilibrium, thermodynamics, acids and bases, bonding and oxidation-reduction reactions. Also knowledge about geological formations and minerals, their structures, physical and chemical properties, and water-rock interactions.

Water chemistry concerns the interaction between geological formations and water. Modern computer programs are used for the interpretation of water samples and the constituents of water, these programs use mathematical model to give the relationship between cations and anions, for example, the relationship between total dissolved solids and electrical conductivity is given by the following formula: $TDS(mg/L) = 0.65 * EC (\mu S)$. Water types, which are indicators for water-rock interactions and gives an idea about the geneses of water, is predicted by Phreeqc, Hydrowin, and Aquachem computer software.

In his book, “Water chemistry: an Introduction to the Chemistry of Natural and Engineered Aquatic Systems”, Patrick Resonik, brings a comprehensive information and basic tools on many topics concerning water chemistry, starting from fundamentals of inorganic and organic chemistry and units of measurement, through natural water chemistry and related subjects like acid-base equilibria, thermodynamics, chemical kinetics, solubility and redox reactions. The author also describes the physical and chemical properties of water and gives principles of water treatment like disinfection, metal ions removal, and organic matter treatment.

In this exam, multiple-choice questions with their answers, are constructed in chapter 1 about the introduction matter, and in chapter 2 about the inorganic composition of natural waters.

Introductory Matters:

Circle the right answer

1- Which of the following bonds responsible for the high boiling point of water
   a- Ionic bond between hydrogen and oxygen in water molecule.
   b- Covalent bonds between hydrogen and oxygen.
   c- Covalent bond between water molecules.
   d- Hydrogen bond between water molecules
   Answer: d
   Hydrogen bond causes more force between water molecules which means more energy is needed to overcome the forces between water molecules.

2- Water is considered a polar compound because:

   a- Oxygen donate electrons to the hydrogen atoms

   b- Hydrogen atoms donate electrons to the oxygen atom

   c- High electronegativity of oxygen draws electrons from hydrogen

   d- Oxygen atom has two unpaired electrons in the outer shell orbital

   Correct answer: C

   Oxygen withdraws electrons more than hydrogen leaving a partial positive charge on hydrogen atoms and causing a negative charge on oxygen atom.

3- Chemical pollutants in water, are measured in units of ppm or ppb; if 2 ppm of lead (Pb) detected in a lake water, this means that the concentration of lead in that lake is:

   a- 2 µg Pb / 10L water

   b- 2 mg Pb/ 1L of water

   c- 2g Pb / 1L water

   d- 2 µg Pb/ 1000 L water

   Answer: b

   Parts per Million (ppm) means 1 part / $10^{\wedge 6}$ parts.

Assuming that the density of water = 1g/ml, so 1 L of water = 1000g= 10^{6} mg

So, 2 ppm = $\frac{2\text{mg}}{10\text{^}6\text{ mg water}}$

4- On a Nestle bottled water has the following information were recorded:

Calcium = 21mg/L Magnesium = 10.3mg/L Sodium = 13.34mg/L

Potassium = 0.37mg/L Chloride = 22.8mg/L Sulfate=8mg/L

Bicarbonate = 96mg/L, and Nitrate = 4.4mg/L

The total hardness expressed as mg/L $CaCO_3$, in Nestlé's bottled water is:

a- 21 mg/L as $CaCO_3$

b- 10.3 mg/L as $CaCO_3$

c- 31.3 mg/L as $CaCO_3$

d- 95.4 mg/L as $CaCO_3$

Answer: d

To calculate the concentration of Ca^{+2} and Mg^{+2} as $CaCO_3$

$[Ca^{+2}] = \frac{21\text{ mg/L}}{40\text{ mg/mmol}} = 0.525$ mmol/L of Ca^{+2}

0.525 mmol/L Ca^{+2} x 2 meq/mmol = 1.05 meq/L of Ca^{+2}

$[Ca^{+2}]$ = 1.05 meq/L x 50 mg /meq of $CaCO_3$ = 52.5 mg /L as $CaCO_3$

$[Mg^{+2}] = \frac{10.3\text{ mg/L}}{24\text{ mg/mmol}} = 0.429$ mmol/L of Mg^{+2}

0.429 mmol/L Mg^{+2} x 2 meq/mmol = 0.858 meq/L of Mg^{+2}

$[Mg^{+2}]$ = 0.858 meq/L x 50 mg /meq of $CaCO_3$ = 42.9 mg /L as $CaCO_3$

Total Hardness= $[Ca^{+2}]$ + $[Mg^{+2}]$ = 95.4 mg/L as $CaCO_3$

5- The solubility of gases in water is calculated according to the formula of:

a- Hess law

b- Fick's law

c- Henry's law

d- Grahams law

Answer: c

Henry's law states that the amount of gas dissolved in water is directly proportional to its partial pressure above the liquid, or $Sw= KHPg$ (Resonik,). S_w is the amount of gas dissolved at certain temperature, P_g is the partial pressure of the gas above the liquid, and K_H is Henry's constant.

6- This reaction is defined as a complex formation reaction

a- $BaCl_{2\,(s)} \rightleftharpoons Ba^{+2}_{(aq)} + 2Cl^{-}_{(aq)}$

b- $HCl + H_2O \longrightarrow H_3O^{+} + Cl^{-}_{(aq)}$

c- $Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$

d- $4Fe^{2+} + O_2 + 4H^{+} \longrightarrow 4Fe^{3+} + 2H_2O$

Answer: c

The reaction between Copper ions and the ammonia ligand is a kind of complex formation reactions.

7- Organic compounds in water bodies, undergo several chemical reactions, which of the following reaction does not match.

a- Hydrolysis reactions

b- Photolysis reactions

c- Redox reactions

d- Pyrolysis

Answer: d

Organic compounds can have hydrolysis reactions in which esters and alkyl halides react with water to form alcohols and carboxylic acids. Organic chemicals in water also use energy from sunlight to turn complicated chemicals into degradable chemicals, such as the reaction of chlorinated herbicides like atrazine with sunlight to produce hydroxyl-atrazine, which biologically degradable compound.

Organic compounds are oxidized in water in the mechanism of electron transfer to form new degradable compound, like the oxidation of alcohols into carboxylic acids, further oxidation of carboxylic acids leads to carbon dioxide and water.

8- Permanent water hardness, which is not removed by boiling , is caused by:

a- Calcium and magnesium carbonates

b- Sodium and potassium carbonates

c- Calcium and magnesium sulfates and chlorides.

d- Zeolite.

Answer: C

Water hardness is a characteristic of water that contains different kinds of salts. Carbonate water hardness, or temporary hardness, is caused by calcium and magnesium carbonates, which is easily removed by boiling of water.

Permanent water hardness is caused by sulfates and chlorides of magnesium and calcium, it can’t be removed by boiling, but it can be removed by water softeners such as soda ash and ion exchange resins such as zeolite.

9- Normality, Molarity and Molality are concentration units that are used by water chemists to express the amount of chemical substances in water. In a solution made by dissolving

56 ml of 97% H_2SO_4 and diluted to 1L. If the density of H_2SO_4 is 1.83g/ml and the formula weight of H_2SO_4 is 98.00 g/mol. The Normality of the solution is :

a- 98N

b- 56N

c- 1.019M

d- 2.028N

Answer: d

Sulfuric acid is a strong acid which dissociates completely in water according to the following equation:

$H_2SO_4 + H_2O \longrightarrow 2H_3O^+ + SO_4^{-2}$

Normality is defined as the number of meq/L of solution; in the above equation, 1 mole of sulfuric acid gives two equivalents of hydronium ions (H_3O^+).

To calculate number of moles in 56ml of sulfuric acid H_2SO_4:

Each ml H_2SO_4 contains .97 g H_2SO_4 SO:

56 ml x0.97x 1.83 g/ml = 99.406 g H_2SO_4

\# Moles of H_2SO_4 = $\frac{Mass\ of\ \mathrm{H}_2\,SO_4}{Formula\ weight\ of\ \mathrm{H}_2\mathrm{SO}_4} = \frac{99.406\ g}{98.00 g/mol}$ = 1.014 moles.

Since the total volumes is on Liter, the Molarity = 1.014M

The Normality is twice the Molarity, so the solution is 2.028N

10- Some organic compounds are biodegradable by bacteria and others are hard be degradable, like aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB's). The process by which oxygen needed to oxidize organic compounds is determined by:

a- Biological Oxygen Demand (BOD).

b- Chemical Oxygen Demand (COD).

c- Volatile Organic Compounds (VOC's)

d- Gas Chromatography (GC)

Answer: b

Organic compounds in water are divided into two categories:

Organic compound that can be degradable by bacteria, the concentration of these compounds is determined by BOD.

The undegradable chemicals, or refractory compounds can be determined by a process called chemical oxygen demand or COD, in which an oxidizing agent like potassium dichromate $K_2Cr_2O_7$ is used to oxidize organic compounds.

Inorganic Composition of Natural Waters:

1- The major cations in natural waters are categorized according to their natural abundance?

a- Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}

b- Ca^{+2},Na^{+}, K^{+}, , Mg^{+2}

c- Mg^{+2}, Ca^{+2},Na^{+}, K^{+}

d- Ca^{+2}, Mg^{+2} , Na^{+}, K^{+}

Answer: d

a- Natural water contains many soluble salts which produce cations and anions. Some of these elements are called major cations such as Ca^{+2}, Mg^{+2} , Na^{+}, K^{+}, and major anions such as bicarbonate HCO_3^{-}, sulfate SO_4^{-2} and chloride Cl-, in some literatures , nitrate NO_3^{-} is considered as a major anion. These cations and anions are derived from natural resources where natural water comes in contact with minerals of geological formations, and they are given the name major cations and anions from their natural abundance. There are other elements found in natural water, but in lower or minor concentrations such as Aluminum, Iron, Manganese, Boron and Silicon.

2- The term sodification of soil, is used when:

a- Very low sodium concentration compared to other cations.

b- Moderate sodium and potassium compared with other major cations.

c- High sodium ratio compared to calcium and magnesium concentrations

d- This term is called on soils rich with silicon oxide.

Answer: c

Sodium ion is considered as conservative ion, which means that it is an unreactive element, although it shares in ion exchange in clays with other elements. In some cases, and due to interference from human activities through uncontrolled disposal of wastewater, which is rich in sodium chloride, in agricultural soil, the Sodium Absorption Ratio (SAR) which is given by the formula: $SAR = \frac{Na^{+}}{\sqrt{\frac{1}{2}(Ca^{+2}+Mg^{+2})}}$, increases which affects the permeability of soil and hence the use of soil for agricultural purposes.

3- It is one of the major anions in water, it is the least reactive anion and considered as a conservative ion, it does not form complexes and it has no acid-base property.

a- Sulfate SO_4^{-2}

b- Chloride Cl^-

c- Nitrate NO_3^-

d- Bicarbonate HCO_3^-

Answer: b

Major anions in water are reactive species, for example bicarbonate is a very reactive anion, it is formed from the hydrolysis of carbon dioxide in water, and it is stable at neutral pH, but it forms carbonates at higher pH, and causes precipitation of calcium carbonate water bodies which is limestone (Bresonik, 2011).

Sulfate is also an active anion, it is reduced in the form of hydrogen sulfide H_2S, which gives the rotten smell to water and is involved in microbial reactions. Sulfate is a strong ligand and forms reacts with some other major ions like calcium and magnesium.

Chloride is the least reactive anion and it is considered as conservative anion, which means that it stays without change. It does not form complexes although it forms chlorides with some trace metal pollutants such as lead, cadmium and zinc (Bresonik, 2011).

4- Skeletal problems , joint stiffness, arthritic symptoms and bone weakness are caused by

a- An increase of calcium ion concentration.

b- A decrease in calcium ion concentration.

c- An increase in fluoride ion concentration.

d- A decrease in fluoride ion concentration.

Answer: c

Fluoride is added to municipal drinking water in small concentrations to prevent tooth decay. An increase in fluoride concentration has an adverse effect on human health, it causes fluorosis.

5- The following reaction is considered as incongruent reaction.

a- $CH_3COOH + H_2O \rightleftharpoons CH3COO^- + H_3O^+$

b- $3BaCl_{2(aq)} + 2Na_3(PO_4)_{(aq)} \longrightarrow Ba_3(PO_4)_{2(s)} + 6Na^+ + 6Cl^-$

c- $CaCO_{3(s)} + H_2O + CO_{2(aq)} \longrightarrow Ca^{+2}_{(aq)} + 2HCO_3^-{}_{(aq)}$

d- $NaAlSi_3O_{8(s)} + H_2O + CO_{2(aq)} \longrightarrow Na^+_{(aq)} + 2HCO_3^-{}_{(aq)} + 2Si(OH)_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)}$

Answer: d

There are two types of dissolution or weathering of minerals, when they come in contact with water; congruent which means that when a mineral dissolved in water, it produces soluble species only, the other type is incongruent dissolution, which means that when a mineral dissolved in water, it produces soluble species and new minerals; the new mineral does not go back to the old mineral. In this reaction, when albite ($NaAlSi_3O_{8(s)}$) is dissolved in water, it produces kaolinite ($Al_2Si_2O_5(OH)_{4(s)}$), and other soluble species.

6- Human activities contribute in the increase of the major ions in water. Fill in the blank spaces the major ions that are induced from the most applicable human activity.

a- Street deicing: -------------------, ------------------

b- Agricultural activities: ------------------, ------------------, -----------------

c- Mining activities: ------------------, -------------------

d- Construction activities: -------------------, ----------------------, ----------------

Answer:

a- Streets deicing: $\underline{Na^+}$, $\underline{Cl^-}$

b- Agricultural activities: P (as phosphate) , $\underline{K^+}$, N (as ammonium or nitrate)

c- Chemical industry: $\underline{Cl^-}$, $\underline{SO_4}^{-2}$, $\underline{Na^+}$

d- Construction activities: $\underline{Ca^{+2}}$, $\underline{HCO_3}^-$, $\underline{SO_4}^{-2}$

Notes: Wastes from chemical industry, produce large amounts of major ions, like sodium hydroxide which is used in dietary industry, Hydrochloric acid and sulfuric acid are used widely industry, they contribute in major ions like chloride and sulfate.

Constructions activities like cutting and building stones contribute in calcium and bicarbonate ions, gypsum and cement contribute in calcium and sulfate ions.

7- Tufa towers are mostly found in:

a- Dead Sea shores, where high concentrations of sodium and chloride ions.

b- Salt lake shores (UTAH), where high concentrations of calcium and carbonate ions.

c- Mono lake- California, where low concentrations of calcium ions and high concentrations of bicarbonate ions.

d- Atlantic Ocean shores, where high concentrations of magnesium and calcium are found.

Answer: c

In some places like Mono lake/ California, the concentration of bicarbonate ions HCO_3^- is very high, compared with calcium ions Ca^{+2} concentration, inspite of this difference in concentrations, saturation of calcium carbonate takes place and towers of limestone, called TUFA are formed. This phenomenon is explained chemically as follows:

The water in Mono lake is very basic pH= 9.65, which means that this water absorbs carbon dioxide from air and this carbon dioxide helps in dissolving the solid calcium carbonate as the following reaction:

$CaCO_{3(s)} + CO_{2(aq)} + H_2O \longrightarrow Ca(HCO_3)_{2\,(aq)}$

The solution becomes rich in aqueous calcium bicarbonate, when it comes in contact with air, the previous reaction reversed and calcium carbonate (limestone) deposits again in the shape of towers.

$Ca\,(HCO_3)_{2\,(aq)} \longrightarrow CaCO_{3(s)} + CO_{2(aq)} + H_2O$

These tower formations of limestone are also seen in many places on Earth like Soreq cave near Jerusalem and in Jeita Grotto cave in Lebanon.

8- What is the common name for the mineral $KAlSi_3O_8$

a- Kaolinite

b- Biotite

c- Orthoclase

d- Sylsite

Answer: c

This mineral is Orthoclase, which is part of potassium- Feldspar (K- Feldspar). It is considered as the source of potassium in some geological formations upon weathering process as shown in the following reaction:

$2KAISi_3O_8 + 2H^+ + 9H_2O \rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+$

Or:

Orthoclase +water → Kaolinite + Silicic acid + potassium (King, n.d)

This reaction of in an incongruent dissolution process, in which a new mineral is formed.

9- In a water sample from a spring in Jericho/ Palestine, the following data in table 1, were obtained from a local laboratory in Ramallah.

Table 1: Hydrochemical data for a spring in Jericho/ Palestine

Ca^{+2}	75.85 mg/L	HCO_3^-	313.5 mg/L
Mg^{+2}	28.7 mg/L	Cl^-	50 mg/L
Na^{+1}	25.3 mg/L	NO_3^-	26.3 mg/L
K^{+1}	2.9 mg/L	SO_4^{-2}	20.5 mg/L
F^-	0.2 mg/L	PO_4^{-3}	0.16 mg/L

Fill the blank spaces in the following questions.

a- The Total Dissolved Solids (TDS) = --------------------

b- The Ionic balance as % value = -----------------

c- The Total Hardness as mg/L CaCO3 = --------------

d- The water type is -----------------------

Answer:

a- TDS = 543.76 mg/L, it is calculated as the sum of all cations and anions.

b- To answer this question :

1- Calculate the meq/L for cations and anions.

2- Multiply the meq/ L by the charge on each ion

3- Sum the value for cations = 7.35

4- Sum the values for anions = 7.42

5- Subtract the lower value from the higher value(steps 3 & 4) = 0.064

6- Dived the difference on the sum of steps 3 & 4 and multiply by 100. = 6.4%

c- To calculate Total Hardness (TH) as mg/L CaCO3 , we do the following steps

1- $[Ca^{+2}] = \frac{75.85\ mg/L}{40 mg/mmol}$ = 1.9 mmol/L of Ca^{+2}

2- 1.9 mmol/L Ca^{+2} x 2 meq/mmol = 3.8 meq/L of Ca^{+2}

3- **$[Ca^{+2}]$** = 3.8 meq/L x 50 mg /meq of $CaCO_3$ = 190 mg /L as $CaCO_3$

4- $[Mg^{+2}] = \frac{28.7\ mg/L}{24\ mg/mmol} \frac{10.3\ mg/L}{24\ mg/mmol}$ = 1.2 mmol/L of Mg^{+2}

5- 1.2 mmol/L Mg^{+2} x 2 meq/mmol = 2.4 meq/L of Mg^{+2}

6- **$[Mg^{+2}]$** = 2.4 meq/L x 50 mg /meq of $CaCO_3$ = 120 mg /L as $CaCO_3$

7- Total Hardness= $[Ca^{+2}]$ + $[Mg^{+2}]$ = 310 mg/L as $CaCO_3$

d- Water type is predicted from the concentration of major cations and anions, in this example, Ca^{+2}- HCO_3^{-}, are the dominant species. Which indicates that Jericho bottled water is in contact with calcite geological formations.

10- Analysis of water samples for hydrochemistry and geochemistry, has been developed greatly in the past two decades. Analysis of water samples in specialized and private labs, is done with big precision and gives accurate and reliable results. Modern instrumentation took the place of wet chemistry experiments. Fill in spaces the exact name of each instrument used for water analysis:

a- ICP-MS:---

b- CIA:---

c- AAS:--

d- FES:---

Answer:

a- ICP-MS: Inductively Coupled Plasma –Mass Spectrometer; this instrument is capable to measure about 50 different cations at the same time with high accuracy. It also can measure different isotopes for different elements. Its running cost is high.

b- CIA: Capillary Ion Analyzer; this is used to measure different kinds of anions with high accuracy and in a short time. Its running cost is low.

c- AAS: Atomic Absorption Spectrometer; used to measure cations and trace elements with high accuracy, it measure one cation at each run. Its running cost is moderate compared with ICP.

d- FES: Flame Emission Spectrometer; used to measure alkali and earth alkali cations such as Sodium, Potassium. Lithium, Calcium and Magnesium. It measures one element at each run, with moderate accuracy, its running cost is very low compared with ICP and AAS.

Conclusion:

It is of great importance for water chemists, environmental engineers, environmental chemists and all scholars who are concerned in environmental issues, to have basic principles in chemistry, so as to be able for interpretation of chemical data and other physical and biological parameters.

After this exam students will have knowledge in basic chemical concepts in water chemistry, chemical pollutants, chemical reactions that are involved in water. Knowledge about concentration units and conversions between units will be acquired. Students will be able to calculate concentrations of different constituents of water and they will be able to give good interpretation for high concentrations of some ions.

This course is very useful for environmental studies' students, as it enriches knowledge in the fields of concern in water purification and treatment and environmental protection.

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