Drinking Water & Wastewater Operator Certification Training



Module 29: General Chemistry

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Topical Outline

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Unit 3 – Solutions

Overview of Solutions Concentration of a Solution Creating Solutions

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Unit 1 – Fundamentals of Chemistry

Learning Objectives

- List the parts of an atom.
- Given the number of protons in an element, indicate its atomic number.
- Given the atomic number of an element, indicate the number of protons in the element.
- Define atomic weight and perform atomic weight calculations.
- Explain the purpose of the periodic table and identify its parts.
- List three states of matter and explain the difference among them.
- List and define four physical properties of matter.
- Explain the difference between elements, compounds and mixtures.
- List the primary differences between a physical and a chemical change of matter

The Structure of Matter

Matter occupies space and has mass. The air that surrounds us, the pencil that we write with and the water that we drink are all examples of matter.

Elements

The fundamental substances of matter are called elements. Examples of elements are aluminum, iron and oxygen. Elements are identified (by a symbol) and arranged in a table called the periodic table.



- The structure of an atom cannot be observed directly due to the extremely small size of the components of an atom.
- All elements are composed of atoms. Atoms are composed of protons, neutrons and electrons. Atoms of the same element are identical. Atoms of different elements have different characteristics.

Atomic Number

The atomic number is equal to the number of protons in an atom's nucleus. The atomic number determines which element an atom is. For example, any atom that contains exactly 20 protons in its nucleus is an atom of calcium.

Protons are a part of the atomic nucleus and have a relatively high mass when compared to electrons. Protons exhibit a positive electrical charge.



Neutrons are a part of the atomic nucleus and have a relatively high mass when compared to electrons. Neutrons have no electrical charge.

Electrons exist outside of the atomic nucleus and have a relatively low mass when compared to protons and neutrons. Electrons have a negative charge.



Figure 1.1 Diagram of an atom

Atomic Weight

The **atomic weight** of an element is a measure of the mass of one atom of the element.

- Atoms are so small that their mass cannot be measured directly. Instead, the atomic weight is a relative scale that compares the mass of an element to the mass of other elements.
- Helium, which has an atomic weight of approximately 4, is about four times as "heavy" as hydrogen, which has an atomic weight of approximately 1.
- Generally, the atomic weight of an element is approximately equal to the sum of protons and neutrons in the element's nucleus.

Periodic Table



Figure 1.2 Calcium as it appears on the periodic table

The diagram above shows a close-up of calcium as it appears on a **periodic table**. Notice the location of the atomic number and symbol.

A Periodic Table a tabular arrangement of the elements according to the nuber of electron shells and chemical properties.

An example of the periodic table is in the appendix. The elements are horizontally arranged according the number of electron shells they have. The horizontal rows are called **periods**. Notice that the vertical columns, called **groups**, tend to have similar chemical properties. What do Chlorine, Bromine and Iodine have in common?

Periodic Table Exercise

- 1. What is the atomic number of an element that contains 11 protons?
- 2. The element Carbon has the atomic number of 6. How many protons does Carbon contain?
- 3. Indicate the atomic weight of an element that contains 7 protons and 7 neutrons.
- 4. Indicate the number of protons and neutrons in an element with an atomic weight of 24.

Classification of Matter

Compounds

As we mentioned before, elements are made of atoms with properties determined by their unique atomic structure.



Most of the matter around us is in the form of compounds. Only a few elements exist in pure form. A compound is a substance that contains two or more elements that are chemically combined. Water is a compound formed from the elements of hydrogen and oxygen. It can also be called a "molecule" of water.



Figure 1.3 Diagram of a water molecule

The elements in a compound are always present in the same proportions. When elements combine to form a compound, the elements lose their individual properties.

Table salt (sodium chloride, NaCl) is another example of a compound. Is O₂ a compound?

No, compounds contain more than one element.

What are some common compounds used in water and wastewater treatment?

What are some elements that are used in water and wastewater treatment?

Mixtures

A mixture is a material that can be separated by physical means into two or more substances. The ingredients of a mixture retain their properties.

- Salt water is an example of a mixture.
- Mixtures can have widely varying compositions. For example, the amount of salt in a salt water solution can vary.
- There are two types of mixtures: heterogeneous and homogeneous.

A heterogeneous mixture is a mixture whose constituent substances are not completely and uniformly mixed throughout the entire mixture.

A **homogeneous mixture** is a mixture whose constituent substances are completely and uniformly mixed throughout the entire mixture.





States of Matter

Matter exists in three states.

- A solid state in which the matter has a fixed shape and a fixed volume. Solid matter is characterized by rigidity. Examples of matter that exist in a solid state include things such as a desk, the floor or even a piece of paper in this workbook.
- A liquid state in which the matter has no fixed shape but has a fixed volume. Liquid matter is a relatively incompressible fluid. Examples of matter in the liquid state include things such as milk, water and gasoline.
- ♦ A gas state in which the matter has no fixed shape and no fixed volume. Matter in the gaseous state is easily compressible. Examples of matter in the gaseous state include hydrogen sulfide, methane, natural gas or the air that we breathe.

Under certain conditions, a material substance can exist in all three states. For example, at room temperature, water is a liquid, but below 32° F, it becomes a solid - ice. If water is heated, it will eventually boil and become a vapor or gas.

Physical Properties of Matter

A physical property is an observable characteristic which does not involve a change in the chemical identity of the material.

Mass

- Mass is the amount of matter present in a given object. It is expressed in units such as pounds (lbs) or grams (g).
- Since mass is the amount of material in an object, it stays the same no matter what force is acting on it. This is what differentiates "mass" and "weight."
- All matter, including chemicals and substances, are commonly described on the basis of "mass."

Weight



Weight is the mass of an object being acted upon by gravity. The weight of an object is proportional to its mass.

There is less gravitational force on the moon than on Earth; therefore, an object on the moon will weigh less than the same object on Earth. The mass of the object remains the same but the weight is different.

Density

Density is the mass of a substance per unit of volume of the substance. All matter has mass and volume; therefore, all matter has a density.

- Density is important because it can be used to relate how a solution compares to water.
- Density is expressed as a mass per volume, such as mg/L or lbs/ft² and is calculated as follows:

Density (d) = <u>Mass (m)</u> Volume (v)

Density of Water

• By definition, 1 Liter of water = 1 kilogram of mass, therefore:

Density of water = 1,000 grams per 1,000 milliliters = 1,000 grams / 1,000 ml = 1 g/ml or 1 g/cm³

- Water has a density of 1 g/ml, 1 g/cm³ or 8.34 lbs/gallon. If you weigh a gallon of water, it will weigh 8.34 lbs. Likewise, if you weigh a milliliter of water it will weigh 1 gram.
- Substances with a greater density will displace those with less density. If a solution has a higher density than water, it will sink in the water; however, if a solution has a lower density than water, it will float on the water. For example, lead will sink in water but oil will float on the water.

Specific Gravity

Specific gravity is the density of a substance compared to the weight of the same volume of water.

- Specific Gravity = <u>Weight</u> Density
- Specific gravity is used to check chemical purity. It is also used to calculate volume for a given weight of chemical or to calculate weight for a given volume of chemical.

Calculating Specific Gravity

- Specific gravity is calculated by comparing the weight of a given volume of a substance to the weight of the same volume of water.
- Water has a density of 1 gram/milliliter (g/ml) so its specific gravity is equal to its density.

Example

Calculate the specific gravity of 1 ml of a substance that weighs 2 grams.

Specific Gravity = <u>Weight</u> Density Specific Gravity = <u>2 gm/ml</u> 1 gm/ml

Specific Gravity = 2

In this example, the substance is twice as dense as water.

Calculating the Weight of a Gallon of Chemical

• To calculate the weight of a gallon of a chemical, multiply the specific gravity of the chemical by the weight of a gallon of water.

Example 1

Calculate the weight of a gallon of 50% NaOH (sodium hydroxide or caustic soda), given that a 50% solution of caustic soda has a specific gravity of 1.53.

Weight, lbs/gal = (Specific gravity of substance) x (weight of a gallon of water)

Weight, lbs/gal = (1.53) x (8.34 lbs/gal)

Weight = A 50% solution of NaOH weighs 12.8 lbs/gal

Example 2

Calculate the number of gallons of 2,000 pounds of 12% NaOCI (sodium hypochlorite), given its specific gravity of 1.12.

Weight, lbs/gal = (specific gravity of substance) x (weight of a gallon of water)

Weight, $lbs/gal = (1.12) \times (8.34 lbs/gal)$

Weight = A 12% solution of NaOCI weighs 9.3 lbs/gal

Calculate the numbers of gallons of 2,000 lbs. of 12% NaOCI

(total weight lbs) / (weight lbs/gallon) = gallons of 12% NaOCI

(2,000 lbs) / (9.3 lbs/gal) = 215 gallons of 12% NaOCI

Changes of Matter

Matter can undergo both physical and chemical changes.

- A physical change in matter is a change in the form of matter but not in its chemical identity. Examples include dissolving and distillation.
- A chemical change in matter is a change in which one or more kinds of matter are transformed into a new kind of matter. Examples include burning or rusting.



Physical and Chemical Changes

Review the following statements and mark whether the change is physical or chemical.

		PHYSICAL	CHEMICAL
1. E v	Drinking water is obtained from ocean water by evaporation and condensation.		
2. 5	Sodium is obtained from sodium chloride.		
3. F	Pulverizing rock salt.		
4. E	Burning wood.		
5. E	Dissolving sugar into water.		
6. F	Rusting of Iron.		
7. T	The evaporation of alcohol.		



Review Exercise

Define the term matter and list the three states of matter.

Differentiate between mass, weight, density and specific gravity. 2.

3. Explain the difference between a physical and a chemical changes in matter.

4. List and define three classes of matter.

Unit 2 – Formulas, Equations and Reactions

Learning Objectives

- Determine the molecular weight of a chemical formula.
- Define mole and calculate the number of moles in a compound.
- Explain the relationship between chemical equations and chemical reactions.
- List and describe four common reactions used in water or wastewater treatment.

Chemical Formulas

- Chemical formulas are the chemist's "shorthand." They are written representations of a compound's components but they do not depict the structure of the molecules.
- Examples of chemical formulas include: H₂O (water), NaOH (sodium hydroxide or caustic soda) and CO₂ (carbon dioxide).
- In order to determine how much of a chemical needs to be added to a solution or how much will be required to create another compound, it is necessary to calculate the molecular weight of compounds.
- The **molecular weight** of a substance is the sum of the atomic weights of all the atoms in the molecule.

Calculating Molecular Weight

Some compounds contain more than one atom of an element. H_2O is an example. When a compound contains more than one atom of an element, all of the atoms must be included in order to calculate the formula weight. The Periodic Table lists the atomic weights of the elements.

Examples

Example 1

What is the molecular weight of NaCl (sodium chloride or table salt) given that the atomic weight of Na is 22.989 and the atomic weight of Cl is 35.453?

The molecular weight of NaCl is:

1 Na atom = 22.2989 1 Cl atom = + <u>35.453</u> NaCl = <u>58.442</u>

Example 2

What is the molecular weight of H_2O (water), given that hydrogen has an atomic weight of 1.0080 and oxygen has an atomic weight of 15.9994?

The molecular weight of H₂O is:

2 H atoms = 2.016 $1 \text{ O atom} = + \frac{15.9994}{18.01}$

Exercises

1. What is the molecular weight of H₂SO₄ (sulfuric acid)?

2. What is the molecular weight of 2 molecules of CH₄ (methane)?

Moles

A mole is a method to discuss how many "molecular weights" of a compound are present for a particular mass of the compound.

- A quantity of compound equal in weight to its molecular weight is a mole.
- The concept of moles is an important component necessary for the calculation and determination of concentrations of chemical solutions. Given the extremely tiny size of molecules and the incredible number of molecules which are present, the mole is the basic unit used to conveniently describe how much of a chemical compound is present.

Calculations

Moles work for any system of weights. For example, the molecular weight of water (H₂O) is 18.0099. To calculate the number of moles, divide the molecular weight by the total number of grams. This means that 18.0099 grams of water is equal to one mole of water, or, in other words:

 $Moles = \frac{Wt \text{ of substance in grams}}{Molecular \text{ wt. In grams}}$ $Moles = \frac{18.0099}{18.0099}$ $Moles = 1 \text{ mol } H_2O$

As another example, sodium chloride (NaCl), also known as table salt, is made using one mole each of Na (sodium) and Cl (chlorine). By adding 22.9898 grams of Na to 35.453 grams of Cl, NaCl is formed. Another option is to add 22.9898 pounds of Na to 35.453 pounds of Cl. Again, NaCl is formed. In either scenario, the proportions of the elements are the same, regardless of whether they are measured in grams or in pounds.



Calculations Using Moles

Calculate the number of moles in 80 grams of NaOH (sodium hydroxide or caustic soda).

2. Calculate the number of moles in 40 grams of H₂O₂ (hydrogen peroxide).

3. Calculate the number of moles in 79 grams of KMnO₄ (potassium permanganate).

4. Calculate the number of grams in 0.5 mol of HCI (hydrochloric acid).

5. Calculate the number of grams in 1 mol of $Fe_2(SO_4)_3$ (ferric sulfate).

Chemical Equations and Reactions

Chemical equations make use of formulas to illustrate chemical reactions. They are a written representation of the reaction that occurs between particular chemicals using their chemical formulas.

An example of a reaction is shown below. Hydrochloric acid reacts with sodium hydroxide (called the reactants) to form the "products" water and salt – saltwater! This is an example of a neutralization reaction. Notice that the number of atoms of each element must be equal on both sides of the equation. This is called a balanced equation. Sometimes the study of the reaction steps and balance of elements is called stoichiometry.

 $HCI + NaOH \rightarrow H_2O + NaCI$

Chemical reactions are the driving force behind all processes, including biological, on earth. Water and wastewater treatment makes use of chemical reactions in many of their processes.

What are some examples of chemical reactions in your treatment processes?

Chemical Reactions Common in Drinking Water and/or Wastewater Treatment

Disinfection

Disinfection is the process desinged to kill or inactivate most microorganisms in water, including essentially all disease-causing bacteria. The most common disinfection process is chlorination.

Chlorine reacts with many elements and compounds. The demand for chlorine by these elements and compounds must be satisfied before chlorine becomes available for disinfection. The point at which chlorine stops reacting with organic and inorganic material is known as the chlorine demand.

Chlorine Reactions in Water

• Free chlorine combines with water to form hypochlorous acid and hydrochloric acid, as shown by the following reaction:

 $CI_2 + H_2O \leftrightarrow HOCI + HCI$

• Depending on the pH, hypochlorous acid may be present as the hydrogen ion and the hypochlorite ion:

 $HOCI \leftrightarrow H^+ + OCI^-$

This is important since HOCI has a greater disinfection potential than OCI. The higher the pH, the greater the percent of OCI. Chlorination is more effective at lower pH's.

Coagulation

- Coagulation is the process resulting from the addition of chemicals to a water supply whereby small non-settleable solids are bonded together, resulting in a heavier floc particle which is capable of settling out of a solution. In chemical equations, a solid precipitate is usually identified by a downward arrow 1.
- Chemicals, known as coagulants, are added to cause the non-settleable solids to destabilize and bond together by neutralizing the electrical charges of the solids.
- Common coagulants include metallic salts, such as aluminum sulfate, ferric chloride and ferric sulfate, and polymers. Coagulation is a reaction occurring between the coagulant and the alkalinity of the water. Alkalinity, a measure of the water's content of carbonate, bicarbonate and hydroxide (always expressed in mg/L of equivalent calcium carbonate), is necessary for the coagulation reaction to occur.

Coagulation Using Aluminum Sulfate (Alum)

Alum is widely used as a coagulant in water treatment. It is available in dry and liquid form. When alum is added to water, it reacts with alkalinity to form insoluble aluminum hydroxide and calcium sulfate and carbon dioxide. The chemical reaction is:

 $AI_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2AI(OH)_4 + 3CaSO_4 + 6CO_2$

In the reaction above, alkalinity is represented as bicarbonate, but could be carbonate or hydroxide. Notice the numbers in front of the products on the right hand side of the equation. These are called coefficients and are used to balance the equation as we discussed previously.

Coagulation Using Ferric Sulfate

Ferric sulfate is a common chemical used for coagulation. When added to water containing colloidal substances with a negative electrical charge, ferric chloride hydrolyzes into ferric hydroxide, Fe(OH)₃, an electropositive, insoluble compound that attracts negatively charged non-settleable colloids.

♦ Fe₂(SO₄)₃ (ferric sulfate) reacts with Ca(HCO₃)₂ (bicarbonate alkalinity) to yield Fe(OH)₃ (iron hydroxide). The chemical reaction is:

 $Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_2 + 3CaSO_4 + 6CO_2$

Chemical Precipitation

Chemical precipitation is the conversion of a dissolved substance into insoluble form by chemical means.

- Chemical precipitation is one of the most commonly used processes in water treatment.
- Many metals are found as cations in water and many will form both hydroxide and carbonate solid forms. These solids have low solubility (will not dissolve) and will either precipitate out of solution or are removed by filtration.

A cation is an atom that loses an electron and is left as a positively charged ion, or particle.

Iron Removal

- The most common form of iron in solution in groundwater is ferrous ion, Fe^{2+} .
- Iron in the domestic water supply can stain laundry and porcelain. The reaction of iron and oxygen creates a reddish precipitate (rust).

Iron Oxidation by Potassium Permanganate

- ♦ Fe²⁺ is oxidized by KMnO₄ (potassium permanganate) to yield Fe(OH)₃ (iron hydroxide) and MnO₂ manganese oxide).
- The chemical reaction is:

 $3Fe^{2+} + 7H_2O + KMnO_4 \rightarrow 3Fe(OH)_{3} + MnO_2 + K_{+} + 5H_{+}$

- This is what is occurring during this reaction:
 - $Fe(OH)_3$ and MnO_2 are insoluble solids that precipitate out of the water or are removed through filtration. Alkalinity is consumed through acid production at the rate of 1.49 mg/l as CaCO₃ (calcium carbonate) per mg/l of Fe²⁺ oxidized.

• The potassium permanganate dose required for oxidation is 0.94 mg per mg of iron.

Unit 3 – Solutions

Learning Objectives

- Describe the characteristics of a solution.
- List the three means of describing the concentration of a solution and differentiate among them.
- Distinguish between creating solutions from standard solutions and creating solutions from dry chemicals.
- Correctly perform percent by weight and percent by volume calculations, dilution calculations and calculations to determine the concentration of solutions.

Overview of Solutions

Description

A **solution** consists of two components in which one of the components is dissolved in the other. In other words, they form a homogeneous mixture. The two components are the solvent and the solute.

The **solvent** is the dissolving medium. In water and wastewater treatment, it is usually water.

The **solute** is the substance being dissolved into the solution and may be solid, liquid or gaseous.

Concentration of a Solution

There are a number of ways to express the concentration of a solution. The most common ways are milligram (mg) per liter (L), percent composition and molarity.

By weight concentration

ratio = amount of solute/amount of solution

For instance, if you were to dissolve exactly 200 milligrams (mg) of sodium hydroxide in 1 liter of water, the concentration of sodium hydroxide would be 200 mg/L.

Remember: The reaction between Sodium Hydroxide and water is exothermic meaning it gives off heat. When dissolving Sodium Hydroxide in water, place container in a cold water bath to dissipate the heat.

Percent Composition

There are two ways to express the concentration of a solution using percent composition -- percent by weight or percent by volume.

Percent by Weight

- The weight of solute divided by the weight of the solution multiplied by 100. Note that the weight of the entire solution, not just the solvent, is used.
- This is usually used when solids are dissolved in liquids.

Example

100 grams of NaCl (sodium chloride or table salt) are dissolved in 250 ml of deionized water. 1 milliliter of water weighs approximately 1 gram. The total weight of the solution is 250 gm (H₂O) + 100 gm (NaCl) = 350 gm Percent by weight = $\frac{100 \text{ mg}}{350 \text{ mg}}$ Percent by weight = 28.6 % solution by weight

Percent by Volume

- The volume of solute divided by the volume of solution multiplied by 100. Note that the volume of the entire solution, not just the solvent, is used.
- This is usually used when liquids are dissolved in liquids.

Example

5 milliliters of $H_2SO_{4 (conc)}$ (concentrated sulfuric acid) are dissolved in 95 mls of deionized water. The total volume of the solution is 95 mls (H_2O) + 5 mls (H_2SO_4) = 100 mls. Percent by volume = $\frac{5 \text{ mls}}{100 \text{ mls}}$ Percent by volume = 5% solution by volume

Remember: Always add acid to water, never add water to acid.

Molarity

Molarity is a measure of the relative strength of solutions. Molarity, or molar concentration, is the number of "moles" of solute dissolved in one liter of solvent. Molarity is the most common way to express concentration and is represented by the abbreviation "M."

Molarity = moles of solute/volume (L) of the solution

Remember from earlier that Moles = <u>Wt of substance in grams</u> Molecular wt. in grams

So Molarity = <u>Wt of substance in grams</u> <u>Molecular wt. in grams</u> L

- The higher the Molarity, the "stronger" the solution.
- An aqueous solution that is 0.15 M NH_3 contains $0.15 \text{ mole of NH}_3$ per liter of solution.

Creating Solutions

Solutions from Standard Solutions

Standard solutions are solutions of a known concentration that are typically used to calculate the concentration of another solution.

- A standard solution will react with the unknown solution. The amount of known solution required to completely react with the unknown solution is then used to calculate the concentration of the unknown solution.
- Examples include hardness titration, alkalinity titration and chlorine determination using an amperometric titrator.

Calculating Unknown Solutions

- To calculate the concentration of an unknown solution, it is necessary to know the volume of the sample and record the number of milliliters of known solution.
- ♦ For example, using an amperometric titrator to determine the amount of chlorine in a sample, the operator would add a specific measured amount of a sample to the titrator and then record the number of milliliters of titrant required to neutralize the chlorine in the sample. Depending on the strength of the titrant (i.e. the known solution) the mg/l of chlorine can be calculated. In some cases, the milliliters of chlorine added equal the mg/l concentration of chlorine in the sample.

Diluting Standard Solutions

Standard solutions are made by adding a known quantity of a pure substance to a known quantity of the solvent. There are three general methods used: weight unit volume, dilution and reaction with a known quantity.

- When using the weight per unit volume method, a very precisely measured amount of the solute is added to a very precisely measured amount of the solvent.
- With the dilution method, a known standard solution is diluted with a very precisely measured amount of a solvent to make a new standard solution.
 - The formula is as follows:

(Initial Concentration) x (Initial Volume) = (Final Concentration) x (Final Volume)

Example 1

Mix 1 liter of 25 mg/l NH₃ standard from a 1,000 mg/l NH₃ stock solution.

(Initial Concentration) x (Initial Volume) = (Final Concentration) x (Final Volume) (1,000 mg/l) x (Initial Volume) = (25 mg/l) x (1,000 ml) Initial volume = $(25 \text{ mg/l}) \times (1,000 \text{ ml})$ (1,000 mg/l) Initial volume = 25 ml Note: Concentration units and volume units must be consistent throughout calculation.

Example 2

Mix 200 ml of 0.1 M H₂SO₄ from concentrated H₂SO₄ solution (18 M)

(Initial Concentration) x (Initial Volume) = (Final Concentration) x (Final Volume) (18 M) x (Initial Volume) = (0.1 M) x (200 ml) Initial volume = $\frac{(0.1 \text{ M}) \text{ x (200 ml})}{(18 \text{ M})}$ Initial volume = 1.11 ml

Solutions from Chemicals

Using the concept of molecular weights and moles, the molarity of solutions can be calculated. This gives an operator the ability to mix chemical solutions from raw materials, such as dry chemicals, instead of simply diluting already created solutions.

Molarity = moles of solute/volume (L) solution

Example 1

What is the molarity of a 50 milliliter solution containing deionized water and 50 g HCI?

- Step 1: Convert grams of HCl to moles. The molecular weight of HCl is 36.4606. Moles of HCl = 50 grams 36.46064 Moles of HCl = 1.37 mol
- Step 2: Calculate the molarity. Molarity of the solution = $\frac{1.37 \text{ mol HCl}}{0.5 \text{ Liter}}$ Molarity of the solution = 2.74 M

Example 2

Calculate the grams of KMnO₄ (potassium permanganate) needed to create a 100 ml solution of 0.5 mol KMnO₄.

Remember Molarity = moles of solute/volume (L) solution

- Step 1: Convert moles of KMnO₄ to grams. The molecular weight of KMnO₄ is 158.04. Grams of KMnO₄ = 0.5 mol158.04 Grams of KMnO₄ = 79 grams in 1 liter of solution
- Step 2: Calculate the molar concentration in 100 ml. Molar concentration = $\frac{79 \text{ grams KMnO}_4}{1 \text{ liter}} \times \frac{1 \text{ liter}}{1000 \text{ ml}} \times 100 \text{ ml} = 1 \frac{1 \text{ liter}}{1000 \text{ ml}}$ Molar concentration = 7.9 grams

Example 3

How many milliliters of 0.10 M NaCl are required to yield 0.20 g of sodium chloride?

- Step 1: Convert mass to moles. Moles = <u>0.20 g NaCl</u> 58.44 g NaCl Moles = 0.003422 NaCl
- Step 2: Calculate the volume of solution which is equivalent to 0.00342 mol of NaCl. Remember Molarity = moles of solute/volume (L) solution

0.10 M NaCl = <u>0.003422 moles NaCl</u> X volume (L) of solutions



Exercises

1. Calculate the Molarity of 12g of NaOH dissolved in 250 milliliters of deionized water.

2. Calculate the grams of $Na_2S_2O_3$ (Sodium Thiosulfate) necessary to create a 10 ml solution of 0.6 M solution.

3. Calculate the Molarity of a solution of 81.1 grams of MgCl₂, Magnesium Chloride, in 1.0 Liter of deionized water.

Unit 4 Acids and Bases

Learning Objectives

- Define the terms acid and base
- Explain the pH scale
- Define alkalinity and state the importance

Acids and Bases

Acidic and basic are two extremes that describe a chemical property. Mixing acids and bases can cancel out or neutralize their extreme effects. A substance that is neither acidic nor basic is neutral.

Acids taste sour, are corrosive to metals, change litmus (a dye extracted from lichens) red, and become less acidic when mixed with bases.

Bases feel slippery, change litmus blue, and become less basic when mixed with acids.

An acid is a substance that when dissolved in water increases the concentration of the hydrogen ion, H⁺. Strong acids, such as hydrochloric and sulfuric, dissociate readily, meaning they release a large concentration of H⁺.

A base is a substance that when dissolved in water increases the concentration of the hydroxide ion, OH-Strong bases, such as sodium hydroxide, dissociate readily meaning the release a large concentration of OH-

pH Scale

Acids and bases are measured on a pH scale.

pH is defined as the negative logarithm (base 10) of the H⁺ ion concentration

 $pH = -log [H^+]$

The pH scale measures how acidic or basic a substance is. The pH scale ranges from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic. A pH greater than 7 is basic.

The pH scale is a log scale, meaning, each whole pH value below 7 is ten times more acidic than the next higher value. For example, pH 4 is ten times more acidic than pH 5. The same holds true for pH values above 7, each of which is ten times more alkaline (another way to say basic) than the next lower whole value. For example, pH 10 is ten times more alkaline than pH 9.

pH is an important measurement in water and wastewater treatment because several processes depend on a specific pH range.

List some processes that are affected by pH.

Below is an example of a pH scale identifying the pH range of several materials.



Alkalinity

Alkalinity is a measure of a water's buffering capacity or the capacity to neutralize an acid. It is not a measure of pH, but a measure of the ability to resist a change in pH. These buffering materials are primarily in the form of bicarbonate (HCO_3^-), and carbonate (CO_3^{-2}), and occasionally hydroxide (OH⁻).

Which form of alkalinity exists depends on the pH. Below pH 4.5, no alkalinity is present. Between pH 4.5 and 8.3 all alkalinity present is in the form of bicarbonate. From pH 8.3 to 9.5 bicarbonates and carbonates are present. At pH 9.5, hydroxide alkalinity appears. Regardless of the form, alkalinity is always expressed as Calcium Carbonate.

Waters with low alkalinity are very susceptible to changes in pH. Waters with high alkalinity are able to resist major shifts in pH. As increasing amounts of acid are added to a water body, the pH of the water decreases, and the buffering capacity of the water is consumed. If natural buffering materials are present, pH will drop slowly to around 6; then a rapid pH drop occurs as the bicarbonate buffering capacity ($CO_3^{2^-}$ and HCO_3^{-}) is used up. At pH 5.5, only very weak buffering ability remains, and the pH drops further with additional acid. A solution having a pH below 4.5 contains no alkalinity, because there are no $CO_3^{2^-}$ or HCO_3^{-} ions left.

Alkalinity not only helps regulate the pH of a water body, but also the metal content. Bicarbonate and carbonate ions in water can remove toxic metals (such as lead, arsenic, and cadmium) by precipitating the metals out of solution.

Measurement of Alkalinity

Alkalinity is measured by titration. An acid of known strength (the titrant) is added to a volume of a treated sample of water. The volume of acid required to bring the sample to a specific pH level reflects the alkalinity of the sample. The pH end point is indicated by a color change. Alkalinity is expressed in units of milligrams per liter (mg/l) of CaCO₃ (calcium carbonate).

Unit 5 – Safety

Learning Objectives

- Locate important information on MSDS Sheets
- Identify proper storage procedures for chemicals
- Identify personal protection equipment and discuss proper usage

MSDS

Due to the sometimes violent nature of some chemical reactions, proper safety procedures should always be followed. Material Safety Data Sheets (MSDS) are always included with chemical purchases and should be carefully reviewed to determine safe handling and storage of chemicals. Further information on chemical safety can be obtained in the Module entitled "Safety." In addition, listed below are examples of supplemental safety and health information sources.

- Federal OSHA at www.OSHA.gov.
- Federal EPA at www.epa.gov.
- The Center for Disease Control (CDC) at www.cdc.gov.
- The National Institute for Occupational Safety and Health (NIOSH) at www.cdc/NIOSH.gov.

The Hazard Communication Law is to ensure "that employees have both a need and a right to know the hazards and identities of the chemicals they are exposed to when working."

- Hazardous Identification (chemical Inventory)
- Material Safety Data Sheets
- Labels and other forms of warning
- Employee Information and training
- Written Hazard Communication Program

Requirements of MSDS

The following is a summery of the requirements of MSDS sheets.

- Chemical manufactures and distributors must provide a copy of a MSDS sheet for each chemical.
- Employers must have a MSDS for each hazardous chemical they use.
- The MSDS must be in English.
- The MSDS must be complete, i.e. no blank spaces in any of the sections.
- If the MSDS is incomplete request a completed one.
- The MSDS must be readily accessible to employees.
- A designated person is to be responsible for obtaining and maintaining the MSDSs.
- Each employee who may be "exposed" to hazardous chemicals when working must be provide information and training prior to working with a hazardous chemical.
- "Exposure" is defined under the rule that "an employee is subjected to a hazardous chemical in the course of employment through any route of entry (inhalation, ingestion, skin contact or absorption, etc) and includes potential (e.g. accidental or possible) exposure.
- Training can be as simple as reading the MSDS and understanding the information.

MSDS Sections

The MSDS sheet contains 16 sections that include the following topics:

- 1. Chemical Product and Company Identification
 - Chemical name
 - Chemical formula
 - Trade names
 - Emergency Phone Numbers
- 2. Composition / Information on Ingredients
 - CAS #, this is like its social security # and is a national Identification number.
 - % By weight, useful when doing chem. feed calculation
- 3. Hazardous Identification
 - Potential health effects
 - Routes of entry in the body
- 4. First Aid
 - How to care for the different routes of entry
 - Eyes, skin contact, inhalation, and ingestion
- 5. Fire Fighting Measures
 - Information on flammability
 - What extinguishing media to use
 - Fire and Explosion hazards
- 6. Accidental Release Measures
 - What personal protection clothing should be worn
 - National response Center if spill exceeds a certain volume by weight
 - Additional information in any transportation emergency
- 7. Handling and Storage
 - What PPE to wear during handling
 - How to store (keep bases away for acids)
 - What container should not be used to store chemicals
 - NPCA-HMIS rating: Health, Flammability, Reactivity,
- 8. Exposure Controls / Protective Equipment
 - Respiratory protection
 - Skin protection
 - Eye protection
 - Engineering controls
 - Physical / chemical Properties
 - Boiling point
 - Vapor pressure
 - Specific Gravity
- 10. Stability / Reactivity

9.

- Stability
- Incompatibility
- Hazardous decomposition
- 11. Toxicological Information
- 12. Ecological Information
- 13. Disposal Considerations

- Must be in accordance with federal, state and local regulations
- 14. Transport Information
 - Hazard class (i.e. corrosive, flammable, etc.)
 - Shipping name
 - Identification #
- 15. Regulatory Information
- 16. Other information

We don't have time to read through each section but we can do a short exercise.

Class Exercise:

We are going use a MSDS to answer questions about a caustic soda (Sodium Hydroxide) spill. You will find an MSDS sheet for Sodium Hydroxide in the Appendix.

- 1. In Which section would you find information concerning the different hazards associated with handling caustic soda?
- 2. What are the possible routes of entry?

3. What information would you look for from the MSDSs, before repairing and metering pump or chemical feed system?

4. Where would you find information about storing Sodium Hydroxide? What are the storage recommendations?

Chemical Storage

As we mentioned before, storage requirements are listed on MSDS sheets. In general:

- Store acids and bases separately.
- Store oxidizers and reducers separately.
- No smoking, drinking or eating when working with chemicals.
- Store carbon in a clean, dry place in single or double rows with access around every stack for inspections.
- Store chlorine in secure areas with leak detection equipment.
- Handle cylinders and containers carefully, insure cylinders and containers are secured (chained) to prevent tipping/rolling.
- First aid kits, safety showers and eyewash stations should be available and easy to access.

Personal Protection Equipment (PPE)

Personal Protective Equipment (PPE) consists of the following:

Respiratory Protection

• This is used to control worker exposure to airborne hazardous materials whenever engineering controls are not feasible or are being implemented. It is important the respirator selected and given to the employee is appropriate for the type and severity of the hazard. The use of respiratory protection should be done in accordance with a comprehensive respiratory protection program that includes fit testing, medical evaluation, respirator selection and respirator maintenance.

Protective Clothing

• Protective clothing typically includes gloves, coveralls, suits and aprons to protect against a variety of hazards including chemical, electrical and thermal.

Head, Eye, Hand and Foot Protection

• This is required whenever there is a potential for physical injury and includes hard hats, safety glasses/goggles, work gloves, chemical resistant gloves and safety shoes.

Once again, the MSDS sheet will indicate the PPE to use. In general:

- When working with chemicals that produce powder or dust (lime, carbon) wear respiratory protection.
- When working with caustic materials such as lime and sodium hydroxide or acidic materials such as sulfuric acid protect skin exposure and wear respiratory protection.
- Wear eye protection whenever working around chemicals.
- When handling chemicals wear gloves and insure glove material is compatible with the chemical.
- Never taste chemicals

SODIUM HYDROXIDE

*1. Product Identification*Synonyms: Caustic soda; lye; sodium hydroxide solid; sodium hydrate
CAS No.: 1310-73-2
Molecular Weight: 40.00
Chemical Formula: NaOH
Product Codes:
J.T. Baker: 3717, 3718, 3721, 3722, 3723, 3728, 3734, 3736, 5045, 5565
Mallinckrodt: 7001, 7680, 7708, 7712, 7772, 7798

2. Composition/Information on Ingredients

Ingredient Hazardous	CAS No	Percent			
Sodium Hydroxide Yes	1310-73-2	99 - 100%			

3. Hazards Identification Emergency Overview

- - -

POISON! DANGER! CORROSIVE. MAY BE FATAL IF SWALLOWED. HARMFUL IF INHALED. CAUSES BURNS TO ANY AREA OF CONTACT. REACTS WITH WATER, ACIDS AND OTHER MATERIALS.

SAF-T-DATA^(tm) Ratings (Provided here for your convenience)

Health Rating: 4 - Extreme (Poison) Flammability Rating: 0 - None Reactivity Rating: 2 - Moderate Contact Rating: 4 - Extreme (Corrosive) Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES Storage Color Code: White Stripe (Store Separately)

Potential Health Effects

Inhalation:

Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Severe pneumonitis may occur.

Ingestion:

Corrosive! Swallowing may cause severe burns of mouth, throat, and stomach. Severe scarring

of tissue and death may result. Symptoms may include bleeding, vomiting, diarrhea, fall in blood pressure. Damage may appears days after exposure.

Skin Contact:

Corrosive! Contact with skin can cause irritation or severe burns and scarring with greater exposures.

Eye Contact:

Corrosive! Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

Chronic Exposure:

Prolonged contact with dilute solutions or dust has a destructive effect upon tissue.

Aggravation of Pre-existing Conditions:

Persons with pre-existing skin disorders or eye problems or impaired respiratory function may be more susceptible to the effects of the substance.

4. First Aid Measures

Inhalation:

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

Ingestion:

DO NOT INDUCE VOMITING! Give large quantities of water or milk if available. Never give anything by mouth to an unconscious person. Get medical attention immediately.

Skin Contact:

Immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician, immediately. Wash clothing before reuse.

Eye Contact:

Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

Note to Physician:

Perform endoscopy in all cases of suspected sodium hydroxide ingestion. In cases of severe esophageal corrosion, the use of therapeutic doses of steroids should be considered. General supportive measures with continual monitoring of gas exchange, acid-base balance, electrolytes, and fluid intake are also required.

5. Fire Fighting Measures

Fire:

Not considered to be a fire hazard. Hot or molten material can react violently with water. Can react with certain metals, such as aluminum, to generate flammable hydrogen gas.

Explosion:

Not considered to be an explosion hazard.

Fire Extinguishing Media:

Use any means suitable for extinguishing surrounding fire. Adding water to caustic solution generates large amounts of heat.

Special Information:

In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode.

6. Accidental Release Measures

Ventilate area of leak or spill. Keep unnecessary and unprotected people away from area of spill. Wear appropriate personal protective equipment as specified in Section 8. Spills: Pick up and place in a suitable container for reclamation or disposal, using a method that does not generate dust. Do not flush caustic residues to the sewer. Residues from spills can be diluted with water, neutralized with dilute acid such as acetic, hydrochloric or sulfuric. Absorb neutralized caustic residue on clay, vermiculite or other inert substance and package in a suitable container for disposal.

US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

7. Handling and Storage

Keep in a tightly closed container. Protect from physical damage. Store in a cool, dry, ventilated area away from sources of heat, moisture and incompatibilities. Always add the caustic to water while stirring; never the reverse. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product. Do not store with aluminum or magnesium. Do not mix with acids or organic materials.

8. Exposure Controls/Personal Protection Airborne Exposure Limits:

- OSHA Permissible Exposure Limit (PEL):

2 mg/m3 Ceiling

- ACGIH Threshold Limit Value (TLV):

2 mg/m3 Ceiling

Ventilation System:

A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved):

If the exposure limit is exceeded and engineering controls are not feasible, a half facepiece particulate respirator (NIOSH type N95 or better filters) may be worn for up to ten times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. A full-face piece particulate respirator (NIOSH type N100 filters) may be worn up to 50 times the exposure limit, or the maximum use concentration specified by the appropriate regulatory agency, or respirator supplier, whichever is lowest. If oil particles (e.g. lubricants, cutting fluids, glycerine, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-facepiece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection:

Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.

Eye Protection:

Use chemical safety goggles and/or a full face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

9. Physical and Chemical Properties

Appearance: White, deliquescent pellets or flakes. **Odor:** Odorless. **Solubility:** 111 g/100 g of water. **Specific Gravity:** 2.13 pH: 13 - 14 (0.5% soln.) % Volatiles by volume @ 21C (70F): 0 **Boiling Point:** 1390C (2534F) **Melting Point:** 318C (604F) Vapor Density (Air=1): > 1.0 Vapor Pressure (mm Hg): Negligible. **Evaporation Rate (BuAc=1):** No information found.

10. Stability and Reactivity

Stability:

Stable under ordinary conditions of use and storage. Very hygroscopic. Can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate.

Hazardous Decomposition Products:

Sodium oxide. Decomposition by reaction with certain metals releases flammable and explosive hydrogen gas.

Hazardous Polymerization:

Will not occur.

Incompatibilities:

Sodium hydroxide in contact with acids and organic halogen compounds, especially trichloroethylene, may causes violent reactions. Contact with nitromethane and other similar nitro compounds causes formation of shock-sensitive salts. Contact with metals such as aluminum, magnesium, tin, and zinc cause formation of flammable hydrogen gas. Sodium hydroxide, even in fairly dilute solution, reacts readily with various sugars to produce carbon monoxide. Precautions should be taken including monitoring the tank atmosphere for carbon monoxide to ensure safety of personnel before vessel entry.

Conditions to Avoid:

Moisture, dusting and incompatibles.

11. Toxicological Information

Irritation data: skin, rabbit: 500 mg/24H severe; eye rabbit: 50 ug/24H severe; investigated as a mutagen.

\Cancer Lists\			
	NTP	Carcinogen	
Ingredient	Known	Anticipated	IARC Category
Sodium Hydroxido (1210-72-2)	 No		Nono
Sodium Hydroxide (1510-75-2)	NO	NO	NOILE

12. Ecological InformationEnvironmental Fate:No information found.Environmental Toxicity:No information found.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information Domestic (Land, D.O.T.)

Proper Shipping Name: SODIUM HYDROXIDE, SOLID Hazard Class: 8 UN/NA: UN1823 Packing Group: II Information reported for product/size: 300LB

International (Water, I.M.O.)

Proper Shipping Name: SODIUM HYDROXIDE, SOLID Hazard Class: 8 UN/NA: UN1823 Packing Group: II Information reported for product/size: 300LB

15. Regulatory Information

\Chemical Inventory Status - Part 1\				
Ingredient	TSCA	EC	Japan	Australia
Sodium Hydroxide (1310-73-2)	Yes	Yes	Yes	Yes
\Chemical Inventory Status - Part 2\				

Appendix

		Canada						
Ingredient		Korea	DSL	NDSL	Phil.			
Sodium Hydroxide (1310-73-2)		Yes	Yes	No	Yes			
\Federal, State & International Regu	ulatio	ns - P	art 1\-					
-	-SARA	302-		SARA	313			
- Ingredient R Catg.	۲Q '	TPQ	List	Chem	ical			
- Sodium Hydroxide (1310-73-2) N	 No 1	No	No		No			
\Federal, State & International Regu	ulatio	ns - P	art 2\-					
Ingredient	CERCLA	-2	RCRA- 61.33	-TS0 8(0	CA- d)			
Sodium Hydroxide (1310-73-2) 1	L000	N	 0	No				
Chemical Weapons Convention: No TSCA 12(b SARA 311/312: Acute: Yes Chronic: No F Reactivity: Yes (Pure / Solid)	o): N Fire: 1	o No Pr	CDTA: essure	No No				

Australian Hazchem Code: 2R

Poison Schedule: S6

WHMIS:

This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

16. Other Information

NFPA Ratings: Health: 3 Flammability: 0 Reactivity: 1

Label Hazard Warning:

POISON! DANGER! CORROSIVE. MAY BE FATAL IF SWALLOWED. HARMFUL IF INHALED. CAUSES BURNS TO ANY AREA OF CONTACT. REACTS WITH WATER, ACIDS AND OTHER MATERIALS.

Label Precautions:

Do not get in eyes, on skin, or on clothing. Do not breathe dust. Keep container closed. Use only with adequate ventilation. Wash thoroughly after handling.

Label First Aid:

If swallowed, DO NOT INDUCE VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen. In all cases get medical attention immediately. *****

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Prepared by: Environmental Health & Safety Phone Number: (314) 654-1600 (U.S.A.)

Appendix

PERIODIC CHART OF THE ELEMENTS																	
IA	IIA	IIIB	IVB	¥Β	ΥIB	YIIB		YIII		IB	IIB	IIIA	IYA	YA	YIA	YIIA	GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	C 12.0112	7 N 14.0067	8 0 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312			_								13 AI 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 CI 35.453	18 Ar ^{39.948}
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn ^{54.9380}	26 Fe 55.847	27 Co 58.9332	28 Ni ^{58.71}	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
85.47	Sr 87.62	Y 88.905	Zr 91.22	ND 92.906	MO 95.94	C	Ru	Rh	Pd	AG	Cd	114.82	Sn	SD 121.75	127.60	126.904	Xe
55 Cs 132.905	56 Ba 137.34	*57 La ^{138.91}	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 OS 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 TI 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	≜89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						
Numbers in parenthesis are mass numbers of most stable or most common isotope. Atomic weights corrected to conform to the 1963 values of the Series $ \frac{58}{140.12} \frac{59}{144.24} \frac{60}{(147)} \frac{61}{150.35} \frac{62}{151.96} \frac{63}{157.25} \frac{64}{158.924} \frac{65}{162.50} \frac{66}{164.930} \frac{67}{167.26} \frac{68}{168.934} \frac{69}{173.04} \frac{71}{173.04} \frac{71}{174.97} $ $ \frac{1}{4 \text{ Actinide Series}} $ $ \frac{90}{10} \frac{91}{10} \frac{92}{10} \frac{93}{10} \frac{94}{10} \frac{95}{10} \frac{96}{10} \frac{97}{10} \frac{98}{100} \frac{99}{100} \frac{101}{101} \frac{102}{103} \frac{103}{101} \frac{102}{103} \frac{103}{101} \frac{103}{100} \frac{103}{101} \frac{103}{100} \frac{103}{101} \frac{103}{100} \frac{103}{101} \frac{103}{100} 10$																	
ADDURAUL	Ser noe nu	mbers.	232	.038 (2	31) 238	3.03 (2	37) (2	42) (24	43) (2	47) (24	47) (2	49) (2	54) (2	53) (2	56) (2	56) (2	57)