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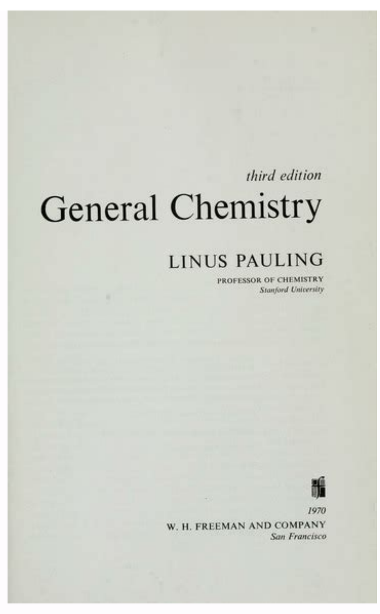
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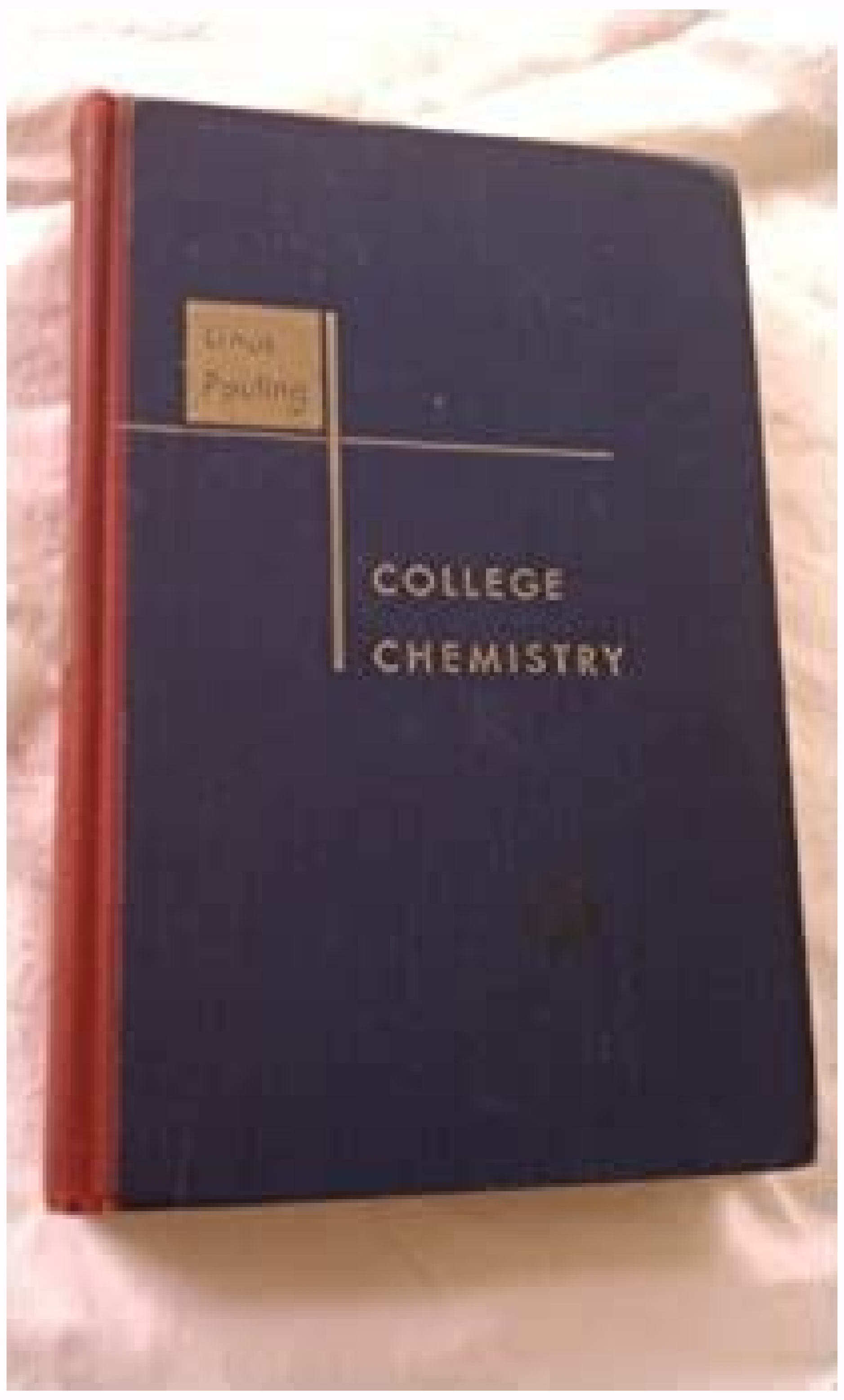
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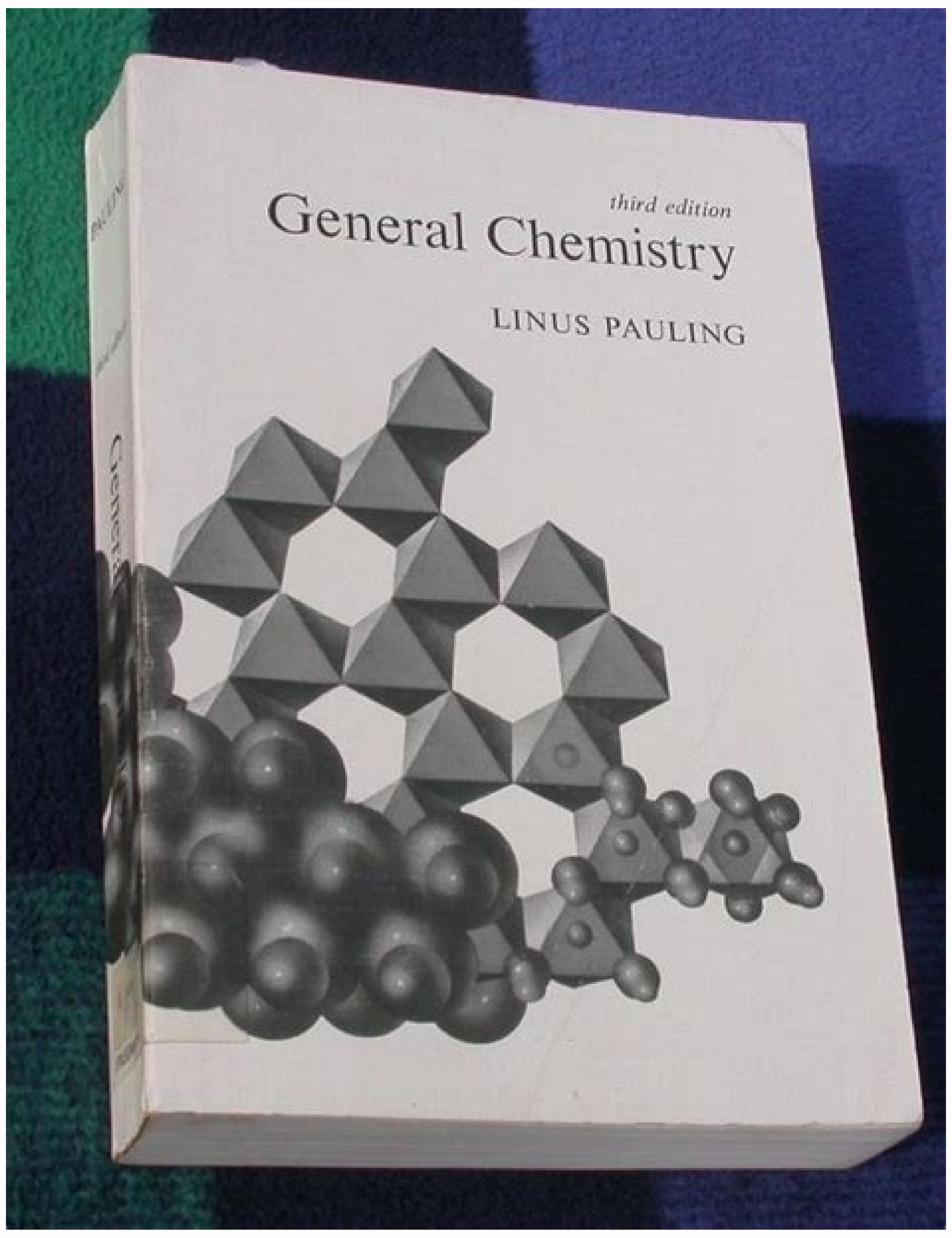
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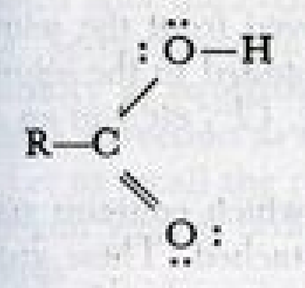
Both the positive ions and the negative ions can be removed from water by a similar method, illustrated in Figure 15-1. The first tank, A, contains grains which consist of giant organic molecules in the form of a porous framework to which acidic groups are attached. These groups are represented in the figure as carboxyl groups, —COOH:



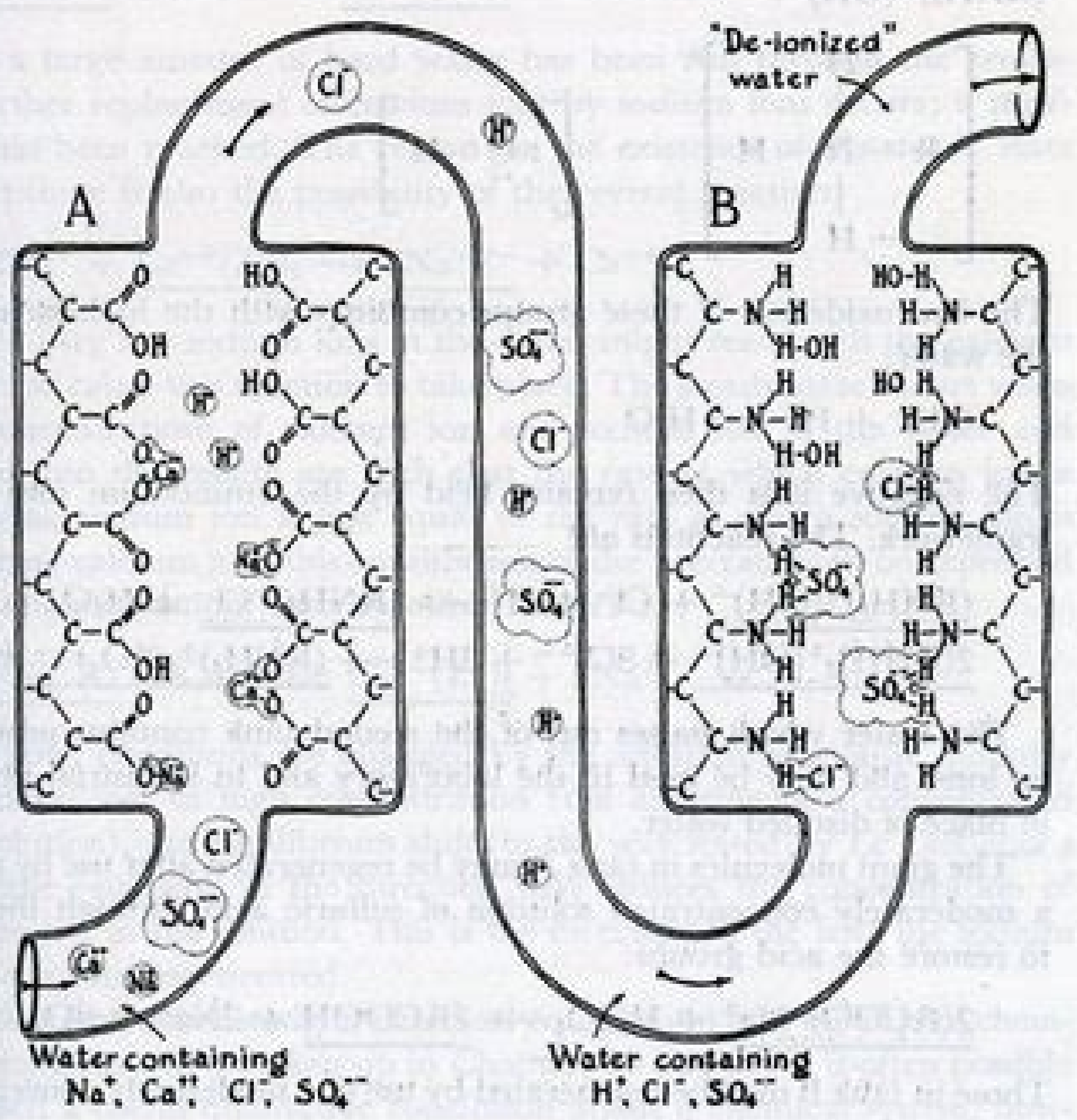


FIG. 15-1 *The removal of ions from water by use of giant molecules with attached acidic and basic groups.*

GENERAL CHEMISTRY

An Introduction to Descriptive Chemistry and Modern Chemical Theory

BY

LINUS PAULING

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ILLUSTRATIONS BY

ROGER HAYWARD

1947

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I regret it! Something went wrong Is your network connection unstable or do you have an outdated browser? 1 Nature and properties of matter 1-1. Matter and Chemistry The universe consists of matter and radiant energy. Matter (from the Latin materia, meaning wood or other material) can be defined as any form of matter-energy (see Chapters 1-2) that moves at a speed less than the speed of light, and radiant energy as any form matter. is energy that travels at the speed of light. Different types of substances are called substances. Chemistry is the science of substances - their structure, properties and reactions that transform them into other substances. This definition of chemistry is too narrow and too broad. This is too narrow because a chemist, when studying matter, must also study the energy of radiation as it interacts with matter. He might be interested in the color of substances obtained by absorbing light. Or he may be interested in the atomic structure of substances as determined by X-ray diffraction (Sections 3-7 and Appendix IV) or the absorption or emission of radio waves by substances. On the other hand, this definition is too broad, as it could cover almost all science. Astrophysicists are interested in substances that are present in stars and other celestial bodies or are distributed in very small concentrations in interstellar space. A nuclear physicist studies the substances that make up the nuclei of atoms. A biologist is interested in substances found in living organisms. A geologist is interested in substances called minerals that make up the earth. It is difficult to draw a line between chemistry and other sciences. 1-2. Matter and Energy Matter has mass, and any piece of matter on Earth is attracted to the center of the Earth by the force of gravity; this attraction is called the weight of a piece of matter. For many years, scientiststhat matter and radiant energy can be distinguished by matter belonging to matter, and non-matter by energy. At the beginning of this century (1905), Albert Einstein (1879-1955) pointed out that energy also has mass and therefore light is attracted to matter by gravity. This has been tested by astronomers who have discovered that a ray of light traveling from a distant star to Earth and passing near the Sun is bent towards the Sun by gravity. The observation of this phenomenon was made during a solar eclipse, when the image of the star was seen near the Sun. The amount of matter associated with a given amount of energy is determined by an important equation, Einstein's equation, which is an essential part of relativity: in this equation, E is the amount of energy (J), m is mass. (kg) ic is the speed of light (m sâ1).* The speed of light c is one of the fundamental constants of nature; its value is 2.9979 × 10–10 meters per second. . Until this century, it was also believed that matter could not be created or destroyed, but only transformed from one form to another. However, in recent years it has been discovered that it is possible to convert matter into radiant energy and turn radiant energy into matter. The mass m of a substance obtained by converting the amount of radiant energy into E or into this amount of radiant energy is given by Einstein's equation. Experimental verification of Einstein's equation was obtained by studying the processes occurring in atomic nuclei. The nature of these processes will be described in later chapters of this book. Until the beginning of this century, scientists used the law of conservation of mass and the law of conservation of energy. These two conservation laws were then combined into one, the law of conservation of matter, where the matter to be conserved includes boththe mass of the system and the amount of radiant energy in the system. 1-3 International System of Units The metric system of length, weight, force and other physical quantities was developed during the French Revolution. Because of their greater convenience and simplicity, metric units have widely replaced the original units (such as feet and pounds) in scientific writing and have been officially adopted for practical use in many countries (all but the United States, Canada, and some African countries).).). An extended and improved form of the metric system called the International System (IS or sometimes SI, for Systéme International) was officially adopted by the General Conference on Weights and Measures in 1960. See Appendix I for symbols for base IS units and prefixes for fractions and multiples and for some derived IS units. If you used cgs (centimeter-gram-second), you will need to learn a few new units. The IS mass unit, kilogram, is defined as the weight of a standard item of platinum-iridium alloy deposited in Paris. A pound is approximately 453.59 grams, so 1 kg is approximately 2.205 pounds. (Note that it has become common to write abbreviations in the metric system without dots.) There is currently a bug in the international system in which the name of the unit of mass includes the kilogram as a prefix. This error will remain until an agreement is reached on a new name and icon. Meanwhile, we must remember that 1 milligram (designation 1 mg, not 1 μg) is one millionth of a unit of mass, and not one thousandth, as indicated by the prefix milli. The unit of length for a meter (m) in IS is approximately 39.37 inches (1 inch equals exactly 2.54 cm). meterformerly defined as the distance between two engraved lines on a standard platinum-iridium bar kept by the Bureau International des Poids et Mesures in Paris; In 1960, by international agreement, it was redefined as 1,650,763.73 wavelengths of the 86 orange-red spectral lines* of the cryptocurrency. The time unit of MC is second (s). It is defined as the interval occupied by 9,192,631,770 cycles of a cesium-133 microwave line* at a wavelength of about 3.26 cm. The second was previously defined as 1/86,400 of a mean solar day. The IS volume unit is the cubic meter, m^3. In chemistry, a unit of measurement - liter, symbol 1, which is equal to 1 × 10 - 3 m^3, is widely used. A milliliter, 1 × 10 - 3 1, is equal to a cubic centimeter: 1 ml \u003d 1 cm^3. The unit of force IS is the newton (N), which is defined as the force required to accelerate a mass of 1 kg by 1 m s^2. A newton is equal to 10 dynamos (the dyne, the CGS unit of force, is the force that accelerates 1 g per 1 cm s 2). The energy unit IS - joule (J) - is the work done by 1 newton at a distance of 1 meter: 1 J = 1 N m = 10 erg = 10 dyn cm. In chemistry, the calorie is widely used as a unit of measurement. energy. The thermochemical calorie, defined as 4.184 J (Appendix I), is approximately equal to the amount of energy required to raise the temperature of 1 g of water by 1 °C. A high caloric content (kcal or cal) is 10^3 cal. In this book, we will use joules in most of the tables and reasoning. Since most reference books on thermochemistry use calories or kilocalories, you will find it helpful to remember the conversion factor: 1-1. example. Niagara Falls (Horseshoe) is 160 feet high. How much warmer is the water at the bottom than at the top because potential energy is converted to heat? The standard acceleration of gravity is 9.80665 m s^2. The decision. The force of gravity per 1 kg of mass on the Earth's surface is 9.80665 N. The change is the potential energy of 1 kg perThe distance h (in meters) is 9.80665 × h J. In this problem, h is 0.3048 × 160 = 48.77 m (conversion factor from Appendix I); therefore, a change in potential energy produces 9.80665 × 48.77 = 478 J of thermal energy. The energy required to raise the temperature of 1 kg of water by 1 °C is given above as 1 kcal = 4.184 kJ = 4184 J. Thus, the increase in water temperature is 478/4184 = 0.114 °C. Example 1-2. When 2 kg of uranium-235 undergoes nuclear fission (as in the atomic bomb explosion at Hiroshima on August 6, 1945), 1.646 × 10^1 J of radiation and heat energy is released. What is the mass of the real products of the reaction? Decision. We can calculate the mass of energy released using Einstein's equation (1-1). If we rewrite this equation by dividing each side by c^2 and substituting the values of E and c, we get: Thus, the mass of a 2 kg material decreased by 0.00183 kg (i.e. 0.0915%), which gives material products reaction. they are left with a mass of 1.99817 kg. Einstein's connection between mass and energy was verified by direct measurement of the mass of products and the energy released in nuclear reactions. Example 1-3. It has been experimentally established that an explosion of 1 kg of glycerol trinitrate (nitroglycerin) releases an amount of energy of 8.0 10 J. What is the mass of the explosion products? Decision. Solve this example in the same way as the previous one. The mass of radiant energy produced by the explosion is obtained by dividing the energy E by the square of the speed of light: thus, we calculate that the mass of the explosion products is 0.999999999911 kg. We see that the mass of the products of this chemical reaction differs very little from the mass of the reactant - so insignificantly that it is impossible to directly detect the change. A change of less than one part in ten billion (1 in $10^{1°}$) is small enough to be practical.we can say that mass is conserved in ordinary chemical reactions. 1-4 Temperature When two objects touch, heat energy can be transferred from one object to another. Temperature is a property that determines the direction of the flow of thermal energy - it flows from an object with a higher temperature to an object with a lower temperature. The temperature is usually measured with a thermometer, such as a conventional mercury thermometer, which consists of some mercury in a glass tube. The temperature scale used by scientists is the Celsius or Celsius scale; it was introduced in 1742 by Anders Celsius (1701–1744), a Swedish professor of astronomy. On this scale, the temperature of freezing water saturated with air is 0 °C, and the temperature of boiling water is 100 °C at a pressure of 1 atm. On the Fahrenheit scale used in everyday life in Anglo-Saxon countries, the freezing point of water is 32°F and the boiling point is 212°F. On this scale, freezing and boiling points differ by 180°, not 100° Celsius*. Celsius, and 0°C is the same temperature as 32°F. The Kelvin temperature scale About 200 years ago, scientists noticed that the volume of a cooled gas sample periodically decreases, and found that if the volume continues to decrease in this way, it will reach zero at about ... 273 °C. . A concept was developed according to which this temperature - 273 ° C (more precisely - 273.15 ° C) is the minimum temperature, absolute zero. A new temperature scale was then developed by Lord Kelvin, the great British physicist (1824-1907). The Kelvin scale is defined in such a way that the laws of thermodynamics can be expressed in simple terms (see Chapter 10). The IS temperature scale is the Kelvin scale with a new definition of degrees. 0°K and the triple point of water are considered absolute zero.(The triple point of water, or the temperature at which pure liquid water, ice, and water vapor are in equilibrium, is discussed in Section 11-9.) Using this definition of degree, the boiling point of water at one atmosphere pressure is 373.15° K, and the freezing point of water saturated with air at one atmosphere* is 273.15 °K. Thus, the temperature in Kelvin is 273.15 K higher than the temperature in degrees Celsius. 1-5 Types of Matter First, let's distinguish between objects and types of matter. An object such as a person, a table, a copper doorknob can be made of a single type of material or multiple types of material. The chemist is not primarily interested in the objects themselves, but in the nature of the matter from which they are made. He is interested in a brass alloy, be it a doorknob or some other object; and may be interested primarily in those properties of the material which do not depend on the nature of the objects that contain it. Materials The word "material" is used to refer to any type of matter, whether homogeneous or heterogeneous. Heterogeneous material is a material consisting of parts with different properties. Homogeneous material has the same properties along the entire length. Wood with alternating soft and hard grains is obviously a heterogeneous material, as is granite, in which grains of three different substances (minerals: quartz, mica and feldspar) can be discerned. A mineral is a chemical element, chemical compound, or other homogeneous material (such as a liquid solution or a crystalline solution) that occurs in nature as a product of inorganic processes. Most minerals are solid. Water and mercury are examples of liquid minerals, while air and helium (from rock or helium wells) are examples of gaseous minerals. An example of a mineral solution is amalgam (mercury containing dissolved silver and gold). Rocks are simple minerals (limestone consists of the mineral calcite, or calcium carbonate) orminerals (granite is such a mixture). Substances A substance is usually defined by chemists as a homogeneous type of matter with a relatively specific chemical composition. According to this definition, the representative substances are pure salt, pure sugar, pure iron, pure copper, pure sulfur, pure water, pure oxygen and pure hydrogen. On the other hand, a solution of sugar in water is not a substance; it is of course homogeneous, but it does not meet the second part of the above definition, because its composition is not defined, but it varies greatly, depending on the amount of sugar dissolved in a given amount of water. Similarly, the gold of a gold ring or watch case is not a pure substance, even if it appears to be uniform. It is an alloy of gold with other metals, usually consisting of a crystalline solution of copper in gold. The word "alloy" is used to refer to a metallic material containing two or more elements: intermetallic compounds are substances, but most alloys are crystalline solutions or mixtures. Sometimes (as in the first part of this chapter) the word "substance" is used in a broader sense, essentially equivalent to material. For the sake of clarity, a narrower chemical meaning can be defined by the expression pure substance. Our definition is imprecise because it says that a substance has a fairly definite chemical composition. Most materials that a chemist calls substances (pure substances) have a definite chemical composition; for example, pure salt is composed of two elements, sodium and chlorine, in the exact ratio of one sodium atom to one chlorine atom. Others, however, show a small range of changes in chemical composition; an example is iron sulfide, which is formed by heating iron and sulfur together. This substance has a composition of a few percent. Types of definitions Definitions can be precise or imprecise. mathematician canthe exact words he uses; in his further discussion he strictly adheres to the defined meaning of each word. We have given some precise definitions above. One of them is the definition of the kilogram as the kilogram weight of a standard object stored in Paris. Similarly, a gram is precisely and precisely defined as 1/1000 of the weight of a kilogram. On the other hand, the words used to describe nature, which is itself complex, may not be precisely defined. In providing a definition for such a word, an attempt is made to describe the accepted usage. Mixtures and Solutions A sample of granite that shows grains of three different types of matter is clearly a mixture. The mixture is also an oil-in-water emulsion (a suspension of oil droplets in water). The heterogeneity of a piece of granite is obvious at a glance. The heterogeneity of an emulsion containing large oil droplets suspended in water is also evident; It is clear that an emulsion is a mixture. But as the oil droplets in the emulsion become smaller and smaller, it may become impossible to observe the heterogeneity of the material and confusion may arise as to whether the material should be called a mixture or a solution. A normal solution is homogeneous; However, due to its variable composition, it is not normally classified as a substance. A solution of liquids such as alcohol and water or gases such as oxygen and nitrogen (the main components of air) can also be called a mixture. The word mixture can therefore denote a homogeneous material that is not a pure substance, or a heterogeneous combination of two or more substances. A homogeneous crystalline material is not necessarily a pure substance. Therefore, natural sulfur crystals are sometimes dark yellow or brown instead of light yellow. Dark crystals contain some amount of selenium randomly distributed in the crystals in placesulfur crystals are homogeneous and have the same face shape as pure sulfur. These crystals are a crystalline solution (or solid solution). The copper-gold alloy used in jewelry is another example of a crystalline solution. It is a homogeneous material, but its composition is variable. Phases A material system (i.e. a limited part of the universe) can be described using the phases of its individual components. A phase is a homogeneous part of a system separated from other parts by physical boundaries. For example, if a flask is partially filled with water in which ice floats, the system consisting of the contents of the flask consists of three phases: ice (solid phase); water (liquid phase); and air (gas phase). Under a microscope, you can see a piece of malleable iron, which is a mixture of fine grains of iron and particles of graphite (a type of carbon); therefore, it consists of two phases: iron and graphite (Fig. 1-1). FIGURE 1-1. Photomicrograph (100x linear magnification, i.e. 100x magnification) of a polished and etched surface of a ductile iron sample showing fine iron grains and coarsely spherical graphite (carbon) particles.). Iron grains look slightly different from each other due to different lighting. (From the Society of Flexible Founders.) A phase in a system includes all parts that have the same properties and composition. Therefore, if there were more pieces of ice in the considered system, they would not form several phases, but only one phase - the ice phase. Additives and Additives Chemists use the words additive and additive in a special way. System components are the different phases that make up the system. A set of system components is a set of substances (minimum number of substances) from which the phases (components) of the system could be composed. The aforementioned system has three componentsair, water and ice. The components of the system can be thought of as air and water or air and ice because both the water phase and the ice phase can be composed of the same substance, water (or ice).* In this case, the number of components is less than the number of phases. There may be more; for example, a system consisting only of a sugar-water solution has one phase, the solution, but has two components, sugar and water. 1-6. Physical properties of substances The properties of substances are their intrinsic properties. Sodium chloride (washing salt) can be selected as an example of a substance. We have all seen this substance in different forms - table salt, in small grains; in the form of salt crystals with a diameter of 2 or 3 mm, for use in restoring water-softening minerals; crystals of natural rock salt with a diameter of 5 cm or more. Despite the obvious difference, all these salt samples share the same basic properties. In each case, the crystals, small or large, are bounded by square or rectangular faces of various sizes, but each face must always be at right angles to each adjacent face. Crystals are characterized by different properties in different directions, especially the formation of facets, edges and vertices. The splitting of different salt crystals is the same: when crushed, the crystals always break (split) along planes parallel to the original surfaces, forming smaller crystals similar to larger ones. Different samples have the same salty taste. Their solubility is the same: at room temperature (18°C) 35.86 g of salt dissolves in 100 g of water. The density (weight to volume ratio) of salt is the same and is 2.163 g cm3. Properties of this type, which are not significantly affected by sample size or distribution state, are called intrinsic properties* of the substance present in the samples. There are other propertiesdensity and solubility, which can be accurately measured and expressed in numbers. Another such property is the melting point, the temperature at which a crystalline substance melts to form a liquid. Electrical conductivity and thermal conductivity are similar properties. On the other hand, there are also interesting physical properties of matter, which are not so simple in nature. One such property is the plasticity of a substance—the ease with which it can be compacted into thin sheets. A related property is plasticity, the ease with which a substance can be drawn into a wire. A similar property is hardness: we say that one substance is less hard than another when it is scratched by another substance, but this test only gives qualitative information about hardness. An overview of hardness is given in Section 7-1. The color of a substance is an important physical property. It is worth noting that the apparent color of a substance depends on the degree of its separation: the color becomes lighter as large particles break down into smaller ones, as the distance that light penetrates before being reflected from the interfaces (surfaces) decreases as how the particles get smaller. It is customary to say that under the same external conditions, all samples of a particular substance have the same specific physical properties (density, hardness, color, melting point, crystal form, etc.). However, sometimes the word "substance" is used to refer to a material regardless of its state of aggregation; for example, ice, liquid water, and water vapor may all be referred to as the same substance. In addition, a sample containing rock salt crystals and table salt crystals can be called a mixture, even though the sample may consist of only sodium chloride. This lack of clarity does not seem to cause confusion in practice.Substance is, of course, an idealization; all real substances are more or less impure. However, it is a useful concept because we have learned from experiments that samples of different impurities with the same major component and different impurities tend to have nearly the same properties when the impurities are present in small amounts. These properties are considered to be properties of an ideal substance. 1-7 Chemical properties of substances The chemical properties of a substance are those properties related to its participation in chemical reactions. Chemical reactions are processes in which one substance is converted into another substance. For example, sodium chloride tends to turn into a soft metal (sodium) and a greenish-yellow gas (chlorine) during electrolysis. It also has the property of forming a white precipitate when dissolved in water with the addition of silver nitrate solution; and has many other chemical properties. Iron tends to combine easily with oxygen in moist air and forms iron rust; while an alloy of iron with chromium and nickel (stainless steel) resists this rusting process. This example shows that the chemical properties of materials are of great importance in engineering. Most substances can undergo many chemical reactions. The study of these reactions forms a large part of the study of chemistry. The properties of taste and smell are closely related to the chemical nature of substances and should be considered as chemical properties; The senses of smell and taste in animals are chemical senses. How molecules of taste and smell substances interact with the nerve endings of the mouth and nose and give rise to the sensations of taste and smell has not yet been studied; this problem, as well as the molecular basis of drug action,solution of the young generation of chemists. 1-8. The Scientific Method An important reason for studying science is to learn the scientific method of solving problems. The method can be valuable not only in the field of science, but also in other areas - business, jurisprudence, management, sociology, international relations. It is not possible to present a complete description of the scientific method in a few paragraphs. Here is a partial interpretation, which is reinforced at the beginning of the next chapter and in subsequent chapters. At this point, I can say that one part of the scientific method consists in applying the principles of rigorous reasoning developed in mathematics and logic, in deriving correct conclusions from a set of accepted postulates. In the field of mathematics, the basic postulates are accepted as axioms, and then the whole subject is deduced from these postulates. In science and other areas of human activity, the basic postulates (principles, laws) are unknown, but they must be discovered. The process of discovering these laws is called induction. The first step in applying the scientific method is curiosity about the world, about the facts discovered through observation and experiment. In our science, these are the facts of descriptive chemistry. The next step is to classify and compare multiple facts with one statement. Such a general proposition, covering a number of facts, is called a law—sometimes a law of nature. Such an attempt to classify facts often involves new experiments revealing new facts. For example, when it was discovered in the early 19th century that water could be decomposed into hydrogen and oxygen using electrolysis (the application of an electric current), quantitative measurements of the amount of hydrogen and oxygen were made. In one experiment, 9 g of water was found to produce 1 g of hydrogen and 8 g of water when electrolyzed.This fact was then supported by other facts for the given sample of water, all of which showed that the same amount of hydrogen, 1g, and the same amount of oxygen, 8g, were obtained by electrolysis of 9g of water from other sources. After many more experiments, all of which led to the same conclusion, the facts were summarized in one law: All samples of water release the same relative amounts of hydrogen and oxygen when electrolyzed. When similar results were obtained for some other substances, this law was generalized to the law of constant composition (or the law of definite proportions): in any pure sample of a given compound, the elements are present in the same mass ratio. It should be noted that the induction process is never completely reliable. If one hundred analyzes of water are carried out (by weighing the amounts of hydrogen and oxygen obtained by electrolysis of water samples from various sources) and the same mass ratio of hydrogen to oxygen is found - within the accuracy of the experiments - it seems reasonable to conclude that all water samples have the same mass ratio of hydrogen to oxygen. However, if a credible analysis were performed showing a different ratio, the law would have to be changed. You may find that the law holds when you weigh gases to within 0.1%, but not when you weigh more accurately. This has been noted with water. In 1929, William F. Giauque (b. 1895) discovered that there are three different types of oxygen atoms with different masses (these atoms are called isotopes; see Chapter 4), and soon after Harold C. Urey (b. 1893) discovered the with two types of hydrogen atoms with different masses. Water is made up of molecules made up of these different types of hydrogen atoms and oxygen atoms and contains hydrogen and oxygen in different forms.by weight and found that the weight composition of pure water from different natural sources actually varies slightly. Therefore, it became necessary to revise the law of constant composition to take into account the existence of these isotopic forms of atoms. How this happens is described in Chapter 4. One important way to achieve scientific progress is through the process of successive approximation. Some measurements are made with a certain accuracy, for example, measurements of the composition of a substance with an accuracy of 1%, and a general law is formulated that covers all these measurements. Then it may happen that more precise measurements reveal deviations from the first law. We can then formulate a second, more subtle but also more complex law that captures these deviations. This procedure may have been carried out several times in formulating the law of nature in its present form. It is wise to remember that a law obtained by induction may at any moment be limited in its validity. Conclusions drawn from such a law by a process of deduction must be considered correct, determined by the probability that the original law is correct. Using the scientific method is not just about applying logical rules and procedures on a daily basis. Often a generalization involving many facts goes unnoticed until discovered by a scientist with extraordinary insight. Intuition and imagination play an important role in the scientific method. As more and more people understand the nature of the scientific method and learn to apply it to solving the problems of everyday life, we can hope for the improvement of social, political and international relations around the world. Technological progress is one way the world can lookthrough learning. Another way is social progress resulting from the application of the scientific method through the development of a science of morality. I believe that the study of science, the study of the scientific method by all people, will ultimately help the people of the world to solve our great social and political problems. Exercise 1-1. What is the difference between matter and radiant energy? 1-2. What is Einstein's relationship between matter and energy? Determine the IS units of the words in this relationship. 1-3. Approximately how much energy in IS units is required to heat 1 liter (1 kg) of liquid water from 273.15 °K to 373.15 °K? (See discussion of calories, section 1-3.) 1-4. Try the following method to convert degrees Celsius to Fahrenheit (or vice versa): add 40, multiply by f (or f), subtract 40. 1-5. Mercury freezes at -40°C. What is its freezing point on the Fahrenheit scale? 1-6. For each of the following systems (i) state how many phases are present in the system; (ii) indicate for each phase whether it is a pure substance or a mixture; iii) identify system components; (iv) provide a set of system components: (a) A flask containing a saturated aqueous salt solution and several salt crystals. b) A 100 ml vacuum-sealed quartz tube containing 10 g of pure zinc is heated until about half of the zinc has melted. (c) Same as (b) but contains 10 g copper/gold instead of 10 g zinc. 1-7. What does an intrinsic property of a substance mean? Are smell, shape, density, color, weight, taste, gloss, surface area, magnetic susceptibility, and heat capacity intrinsic properties? Which of the following properties can be quantified? *For an overview of measurement units, see chapter 1-3. - The symbol c represents the speed of light in empty space. * This line corresponds to the transition of the atom from the state marked 5d5 to the state2p10, each with J = 1. In this transition, the electron drops from the 6d orbital to the 5p orbital (see Section 5-3). * The normal cesium state includes an unpaired electron in the 6s orbital, symbol 2SÂ½. Cesium 133 nucleus has a spin, the spin quantum number has the value 1 = 7/2. The nuclear spin angular momentum and the electron angular momentum add up to a resulting angular momentum corresponding to either the value F = 4 or the value F = 3 of the total angular momentum quantum number. The 3.26 cm line includes the transition between these two levels (see Section 26-7). â A liter used to be defined as the small difference between a milliliter and a cubic centimeter (1 old milliliter = 1.000027 cm3). â¡ Usually pronounced as a rhyme with a shout. * The Fahrenheit scale was developed by Gabriel Daniel Fahrenheit (1686-1736), a natural philosopher born in Gdańsk and living in Holland. In 1714 he invented the mercury thermometer; Previously, alcohol was used as a liquid in thermometers. He considered the zero point of his scale to be the lowest temperature he could reach by mixing equal quantities of snow and ammonium chloride. He chose 212° for the boiling point of water so that his body temperature would be 100° F. The normal temperature of the human body is 98.6° F; Perhaps Fahrenheit had a slight fever when he calibrated the thermometer. â Another absolute scale, the Rankine scale, is sometimes used in engineering in English-speaking countries. It uses degrees Fahrenheit and has a temperature of 0°R at absolute zero. * The definition of 0°C (and 32°F) is that it is the freezing point of water saturated with air at one atmosphere of pressure. This temperature is 0.010 °K lower than the triple point temperature. Increasing the pressure from the triple point value of 0.00603 atm to 1 atm lowers the freezing point by 0.0075 °K and the presence of dissolved air.and oxygen) reduces it by another 0.0024°K. * In the above discussion, air was described as a component of the system. It would not be difficult to discuss the change in a system where air behaves like nitrogen, but with a rigorous treatment, air may need to be described as containing multiple components (nitrogen, oxygen, argon, etc.). * Also called specific characteristics. 2. Atomic and molecular structure of matter. The properties of any kind of matter are most easily and clearly compared and understood when they are related to its structure, taking into account its constituent molecules, atoms and even smaller particles. This topic, the atomic structure of matter, is covered in this chapter. 2-1 Hypotheses, Theories, and Laws When an idea is first found to explain or correlate a set of facts, the idea is called a hypothesis. A hypothesis can be subjected to further testing and its conclusions can be tested experimentally. If it continues to agree with the results of the experiment, the hypothesis is called a theory or law. A theory, such as atomic theory, usually contains an idea about the nature of some part of the universe, while a law can be a general statement of observable experimental facts. For example, there is a law of constant angles between crystal surfaces. This law states that whenever the angles between the corresponding faces of different crystals of a pure substance are measured, they have the same value, whether the crystal is small or large. It does not explain this fact. An explanation for this fact comes from the atomic theory of crystals, the theory that atoms in crystals are arranged in the correct order (as discussed later in this chapter). Chemists and other scientists use the word theory in two slightly different senses. The first meaning of this word has been described above, vizA hypothesis that was confirmed. A second use of the word theory is to represent a systematic body of knowledge consisting of facts, laws, theories in the limited sense described above, deductive reasoning, and so on. So by atomic theory we mean not only the idea that matter is made up of atoms, but also all the facts about matter that can be explained and interpreted in terms of atoms, as well as the arguments that have been developed to explain the properties of matter. certain conditions. their atomic structures. 2-2 Atomic Theory In 1805, the English chemist and physicist John Dalton (1766-1844) hypothesized that all substances are composed of small particles of different types of matter corresponding to different elements. He called these particles atoms, from the Greek word atomos, meaning indivisible. This hypothesis provided a simple explanation or picture of the previously observed but unsatisfactorily explained relations between masses of substances participating in chemical reactions with each other. As further work in chemistry and physics confirmed, Dalton's atomic hypothesis became the atomic theory. The rapid development of our science in this century is well illustrated by the increase in our knowledge of atoms. A popular early 20th century chemistry textbook defined atoms as imaginary entities whose bodies are aggregates. An article on the atom in the 11th edition of the Encyclopaedia Britannica, published in 1910, concluded: The atomic theory has been invaluable to chemists, but not once in the history of science has a hypothesis, useful in the discovery and coordination of knowledge, been abandoned and replaced by another with later discoveries. Some great chemists thought that such a fate might befall the atomic theory... But modern discoveries in the field of radioactivity doin favor of the existence of the atom, although they lead to the belief that the atom is not such an eternal and immutable thing as Dalton and his predecessors imagined. Now, only half a century later, we have precise knowledge of the structure and properties of atoms and molecules. Atoms and molecules can no longer be considered imaginary. Dalton's arguments in support of the atomic theory The Greek philosopher Democritus (c. 460-370 BC), who took some of his ideas from earlier philosophers, argued that the universe consisted of emptiness (vacuum) and atoms. Atoms were believed to be eternal and indivisible—absolutely tiny, so tiny that they could not be reduced in size. He believed that the atoms of various substances, such as water and iron, were essentially the same, but differed in some superficial way; water atoms, which are smooth and round, would tumble over each other, while iron atoms, which are rough and jagged, would stick together to form a solid. Democritus' atomistic theory was pure speculation and too general to be useful. However, Dalton's atomic theory was a hypothesis that explained many facts in a simple and reasonable way. In 1785, the French chemist Antoine Laurent Lavoisier (1743-1794) clearly showed that no measurable mass changes occur during a chemical reaction: the mass of the products is equal to the mass of the reactants. In 1799, the French chemist Joseph Louis Proust (1754-1826) formulated another general law, the law of constant proportions. The law of constant proportions states that different samples of a substance contain its elementary components (elements) in equal proportions. For example, analysis revealed that the two elements hydrogen and oxygen are present in any water sample in a 1:8 mass ratio. Dalton assumed that elements are composed of atoms, and that all atoms of one element are identical, and that compoundsfrom combinations of atoms of two or more elements, each in a certain number. In this way, he was able to explain in a simple way the law of conservation of mass and the law of constant proportions. A molecule is a group of atoms bonded together. If a water molecule is formed by combining two hydrogen atoms with one oxygen atom, then, according to the law of conservation of mass, the mass of the molecule must be the sum of the masses of two hydrogen atoms and one oxygen atom. The specific composition of the compound is then explained by the specific ratio of atoms of different elements in the molecules of the compound. Dalton also formulated another law, the simple law of multiple proportions*. This law states that when two elements combine to form more than one compound, the mass of one element combining with the same mass of the other is in small integer ratios. It was experimentally found that one carbon monoxide consists of carbon and oxygen in a weight ratio of 3:4, and the other carbon and oxygen in a ratio of 3:8. The mass of oxygen together with the same mass of carbon, 3g, is 4g and 8g in both substances; that is, they are related to the small integers 1 and 2. This relationship can be explained by assuming that the second substance combines twice as many oxygen atoms with the same number of carbon atoms as the first. Dalton had no way of determining the correct compound formulas and arbitrarily chose the formulas to be as simple as possible; for example, he assumed that the water molecule was composed of one hydrogen atom and one oxygen atom, when in fact it was composed of two hydrogen atoms and one oxygen atom. 2-3 Modern methods of studying atoms and molecules In the second half of the 19th century, chemists began to discuss the properties of substances on the basis of accepted molecular structures. Accurate information about the atomic structureand crystals of many substances were finally obtained in the last period, starting from 1912. Physicists have developed many effective methods for studying the structure of matter. One of these methods is the interpretation of the spectra of matter (see Fig. 21-1). For example, a flame containing water vapor emits light characteristic of a water molecule. The spectrum of water vapor can be observed when this light passes through a spectroscope. Linear measurements were made and interpreted in the spectrum of water, and it was found that the two hydrogen atoms in the molecule are about 97 pm (or 97 x 10 x 12 m) from the oxygen atom. In addition, it was shown that the two hydrogen atoms are not on opposite sides of the oxygen atom, but that the molecule is bent and three atoms form an angle of 104.5°. Spectroscopic methods have been used to determine the distances between atoms and the angles formed by atoms in many simple molecules. The structure of many substances was also established by the methods of electron diffraction and X-ray diffraction. On the following pages we will describe many of the atomic structures that have been determined by these methods. The X-ray diffraction method for determining the crystal structure is discussed in Appendix IV. It was established above that in a water molecule two hydrogen atoms are located at a distance of 97 pm from an oxygen atom. This use is governed by the international system. However, in the past the angstrom* was used as a unit of length to describe interatomic distances; 1=10-8cm=10-10m=100pm. Because of the advantage of the angstrom when discussing interatomic distances and its use in textbooks, we will use it throughout the book. The distance between hydrogen and oxygen in a water molecule is 0.97 Å, and the length of most bonds in molecules and crystals is from 1 ¼ to 4 ¼. 2-4. Arrangement of atoms inCrystal Most solids are crystalline in nature. Sometimes the particles of a solid sample are themselves single crystals, such as cubic crystals of sodium chloride in common salt. Sometimes these individual crystals are very large; sometimes in nature there are crystals of minerals with a diameter of several meters. In our discussion, we will use power as an example. Copper crystals with edge sizes up to a centimeter, as shown in Figure 2-1. found in copper ore deposits. An ordinary piece of metallic copper does not consist of a single crystal of copper, but of a collection of crystals. The crystal grains of a metal sample can be clearly seen by polishing the surface of the metal and then lightly etching the metal with acid. Often the grains are small and can only be seen under a microscope (Figure 2-2), but sometimes they are large and easy to see with the naked eye, such as in some brass doorknobs. 2-1. PHOTO Natural crystals of copper. 2-2. DRAWING The surface of a polished and pickled piece of cold-drawn copper rod showing the tiny crystals that make up the base metal. Magnification 200X (linear x 200). Small round spots are gas bubbles. Experiment (Sections 2-5) showed that each crystal is composed of atoms arranged in a three-dimensional order that repeats itself regularly. In a copper crystal, all atoms are similar and arranged as shown in Figures 2-3 and 2-4. In this way it is possible to pack balls of the same size so that they take up as little volume as possible. This structure, called the structure with the largest cubic packing, was attributed to the copper crystal by W. L. Bragg in 1913. It is the regularity of the arrangement of atoms in the crystal that gives it its characteristic properties, especially the ability to grow. in the form of polyhedrons. (A polyhedron is a rigid body bounded by flat faces.) The faces of a crystal are given byLayers of atoms shown in Figures 2-3 and 2-4. These surfaces are at an angle to each other and have certain characteristic values that are the same for all samples of the same substance. The main layers of the copper surface correspond to the six faces of the cube (cubic or matrix faces); these faces are always perpendicular to each other (at right angles). Eight smaller surface layers obtained by cutting off the corners of a cube are called octahedral faces. Natural copper found in copper ore deposits often occurs as cubic and octahedral crystals (Figure 2-1). 2.3. FIGURE Arrangement of atoms in a copper crystal. A small cube containing four copper atoms is a structural unit; repeating gives you the whole crystal. Figure 2-4 Another atomic view of a copper crystal showing small octahedral faces and large cubic faces. Atoms are not hard balls, they are soft, which allows them to be squeezed (squeezed) harder with increased force. Such compression occurs, for example, when a copper crystal becomes slightly smaller under increased pressure. The quantities assigned to the atoms correspond to the distances between the center of an atom and the center of a neighboring atom of the same type under standard conditions. The distance from a copper atom to each of its twelve nearest neighbors in a copper crystal is 2.55 Å at room temperature and atmospheric pressure; This is called the diameter of the copper atom in metallic copper. The radius of a copper atom is half that. 2-5 Describing Crystal Structure Chemists often use observed crystal shapes to help identify compounds. Describing the shapes of crystals is the subject of the science of crystallography. A method discovered in 1912 by the German physicist Max von Laue (1879-1960) to study the structure of crystals by X-ray diffraction.In recent decades, the work of the English physicists W. G. Bragg (1862-1942) and W. L. Bragg (b. 1890) has acquired particular value. Much of the information on molecular structure presented in this book has been obtained using X-ray diffraction. The description of a crystal structure is based on a structural unit, often called a unit cell. In cubic crystals, the unit cell is a small cube which, when repeated parallel to itself to fill the space, represents the entire crystal. How this happens can be seen in a two-dimensional example. On fig. 2-5 show part of a structure based on a square grid. The structural unit of this square grid is the square; when this square is repeated parallel to itself so as to fill the plane, we get a kind of two-dimensional crystal. In this case, there is one type of atomic lattice, represented by small spheres at the intersections of the lattice lines, and another type of atomic lattice, represented by larger spheres at the centers of the unit squares. It is customary to describe the structure in terms of x and y coordinates, which define the position of the atoms relative to the origin at the corner of the unit cell, and x and y are taken as part of the unit edges of the structure, as shown in the figure. The atom represented by the small sphere has coordinates x = 0, y = 0, and the atom in the center of the square has coordinates x = ½, y = ½. 2-5. FIGURE Arrangement of atoms in a plane. The unit of construction is a square. Small atoms have coordinates 0, 0 and large atoms have coordinates . Similarly, the unit cell of a cubic crystal is a cube which, when played in a parallel orientation, fills space to form a cubic lattice, as shown in Fig. 2-6. on the picture. The unit cell of a given cubic crystal can be described by specifying the value and edge of unity, as well as the values of the x, y, and z coordinates.Atom as part of a unit edge. Thus, for metallic copper, a cubic structure, the structural unit is a cube of side length a Â 2.55 Å and containing four atoms per unit, with coordinates x = 0, y = 0, z = 0; x = 0, y = 1/2, z = 1/2 x = 1/2, y = 0, z = 1/2 and x = 1/2, y = 1/2, z = 0 as shown in 2-7. in the picture. Often these coordinates are written without specifying the symbols x, y, and z; then say there are four copper atoms in the unit at 0, 0, 0; 0; Â½, Â½;, Â½, 0, Â½;, Â½, Â½, 0. 2-6. FIGURE A simple cubic arrangement of atoms. The structural unit is a cube with one atom per unit with coordinates 0, 0, 0. The unit cube shown in Fig. 2-7. In the figure, the coordinates place the atom in only one of the eight corners. Of course, when this unit cube is surrounded by other unit cubes, atoms are located at seven additional corners, and these atoms are formally bonded to neighboring unit cubes. 2-7 FIG. The cubic structure unit for the face-centered cubic arrangement corresponds to the cubic close-packed sphere arrangement. There are four atoms in the unit with coordinates 0, 0, 0; 0; Â½, Â½;, Â½, 0, Â½;, Â½, Â½, 0. The structural unit of the most common type of crystal, the triclinic crystal (see Appendix III and Figure III-4), is a general parallelepiped, as shown in Figure 2-8. This can be described by giving the values of a, b, and c, the lengths of the three sides, and the values of Î±, Î², and Î³, the angles between pairs of sides. FIGURE 2-8 Block representing a general structural unit. It is determined by the length of its three sides and the three angles between the sides. Also shown is a rectangular parallelepiped with light lines on both sides lying in the same plane. Example 2-1. Metallic iron is cubic, with a = 2.86 Â and with two iron atoms per unit cube, at 0, 0, 0 and ½, ½, ½. How many nearest neighbors does each iron atom have and how far apart are they? Solution. We draw the cubic unit of the structure with an edge of 2.86 Â as shown in the figureFigure 2-9 shows the positions 0, 0, 0 and ½, ½, ½. When these types of dice are played side by side, we see that we get the structure shown in Figure 2-10; this is called the body-centered system. You can see that the atom in ½, ½, ½ is surrounded by eight atoms, the atom in 0, 0, 0 and seven similar atoms. Also, the atom at 0, 0, 0 is surrounded by eight atoms. The surrounding atoms are located at the corners of the cube. This situation is described by saying that each atom in the body-centered system has a ligation of 8 (or coordination number of 8). Figure 2-9 Structural unit corresponding to a body-centered cubic system. There are two atoms in the unit with coordinates 0, 0, 0 and ½, ½, ½. FIGURE 2-10 A stereoscopic view of the body-centered cubic structure found for iron and several other metals. [The stereo drawings in this book can be viewed by looking at the right drawing with the right eye and looking at the left eye a few inches from the left drawing. It can be helpful to hold a piece of stiff paper between the drawings. It may take the viewer some time to learn to integrate the two images.] To calculate the interatomic distance, note that the square of this distance equals $(a/2)^2 + (a/2)^2$ + (a The distance between each iron atom and its neighbors is therefore 1.732 × 2.86 × 2 = 2.48 × 1. The metallic radius of iron is therefore 1.24 × 2. Example 2-2 English mathematician and astronomer Thomas Harriot (1560 -1621), who was teacher of Sir Walter Raleigh, who traveled to Virginia* in 1585, was interested in the atomic theory of matter. He believed that the hypothesis that matter was composed of atoms was plausible and explained some of the properties of matter could state the following: "9 solid bodies have atoms in contact with all Syd 10. All homogeneous bodies consist of atoms of similar number and number 11.Mass can be increased by inserting smaller atoms into the gaps between larger ones. 12. From differences in regular (solid) contact we find that the lightest are those with each atom touching six others, and the greatest (if not mixed) when twelve others touch each atom. What would be the difference in density between the two structures described in statement 12 above if represented as hard spheres touching? Decision. A structure in which each atom is in contact with the six others around it, Harriot probably referred to the simple cubic structure shown in Fig. 2-11. In this atomic arrangement, the structural unit is a cube with one atom to which the coordinates 0, 0, 0 can be assigned. Each atom is in contact with six other atoms that are at a distance d from it. cube volume unit