

INORGANIC CHEMISTRY

What does Chemistry study?

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Until recently, the answer on this question was pretty straightforward.

Chemistry is a science dealing with the structure, properties and interconversion of substances.

However, with the advent of new branches of chemistry such as biochemistry, geochemistry, physical chemistry, chemical physics etc, the borders of the realm of chemistry become somewhat blurry, however, by and large, the above definition remains valid. This definition contains one word that is not intuitively clear; this word is “substance”. Let’s discuss it in more details.

1 Chemical substances.

1.1 Physical bodies and chemical substances.

The world around us is full of what we call “material objects”. Each of them can be characterized by coordinate (position in space), size, mass, volume, shape (if they are solids), surface (if they are liquids or solids), etc. When we consider such an object as a single entity (i.e. we do not go into the details of its internal structure), we call it physical body (or physical object). All physical objects are composed of some material (or matter), which can be either homogeneous or heterogeneous. What does that mean? Let’s look at the piece of granite. Granite is a mineral with a granular structure (actually, the Latin word “granite” means “granular”), and if you look at the surface of granite, for example at a granite countertop, you can clearly see colorless semi-transparent grains, non-transparent white or colored grains, and highly brilliant sheet-like threads. These three components of granite can be separated; moreover, they also exist in nature as separate minerals called quartz, feldspar, and mica, accordingly. That means different regions in a piece of granite have different properties and different nature. In other words, granite is *heterogeneous* (in Latin this word literally means “of non-uniform nature”). In contrast, as soon as you

identified a grain of quartz within a piece of granite, every part of this grain will have the same properties, and these properties will be indistinguishable from the properties of quartz obtained from other sources (for example, from sources of natural quartz). Quartz, mica, feldspar, and other materials of that type are called *homogeneous* (i.e. “of uniform nature”) substances.

Homogeneous substances are what chemistry primarily deals with.



Figure 1: Granite (top) and its components: mica (left), feldspar (center), and quartz (right)

1.2 Extensive and intensive properties

. To describe some object or substance means to describe a set of its properties. When we are describing the properties of some physical object, it is logical to start with the description of its size and shape. Obviously, a one kilogram copper ball and a two kilogram copper ball are two different objects with different properties (for example, with different masses). However, from the chemist’s point of view the properties of these two objects are identical: when you put them into an kiln, they melt at the same temperature, if you heat them further, they start to boil at the same temperature too. They have the same hardness and the same electrical resistance. If you decide to cut them onto smaller pieces, the melting and boiling points of such pieces, their density, specific heat capacity will remain unchanged.

The properties that depend on the size of some object are called *extensive*, whereas the properties that are size-independent are called *intensive*.

Obviously, when we are describing physical bodies (objects) we use mostly extensive (size dependent) characteristics, whereas the properties of substances (i.e. the materials these objects are composed of) are intensive.

1.3 Physical and chemical properties of substances.

1.3.1 Physical properties.

We know that water freezes at 0°C and boils at 100°C ; its density is 1 g per cubic centimeter, its specific heat capacity¹ is $4181.3\text{ J}/(\text{kg}\cdot\text{K})$, and its refractive index² is 1.333 (*Frankly speaking, even if you didn't know that before, don't worry, that is not too important for now*). If we decide to determine some of the above properties of water, no water will be lost (i.e. converted to another substance during such measurement). Indeed, we can cool water below 0°C to observe its freezing, but the ice that we obtain is just another state of water, and it will thaw back when heated to room temperature. We can put water into a *refractometer*³ to measure how fast does light propagates in it, but water will remain unchanged during such an experiment. The same is true for all other properties of water listed above (as well as for many other properties of that type). These properties are the properties of water itself, and they are called ***physical properties*** of water. A set of physical properties serves a characteristic of each substance; it is the substance's "fingerprint".

1.3.2 Chemical properties.

It is also known that water, when mixed with quicklime⁴ forms slack lime. When water vapors come into contact with hot iron, two new substances, the iron rust, and a hydrogen gas are formed. When water is added to burning magnesium metal, a burst of fire occurs, and lustrous and compact piece of magnesium metal turns into a white voluminous powder. During all these processes water disappears, and some new substances are generated instead. The ability of some substance to interact with another substance (or substances) to produce new substances, as well as the ability of a substance to decompose (to give new substances) is called a ***chemical property***.

Physical properties are used by chemists to characterize newly discovered substances or to identify already known ones.

Chemical properties of substances are what Chemistry studies.

1.4 Pure substances and mixtures.

If different substances have different physical properties, they can be easily separated when they are mixed together. Thus, when a thin powder of charcoal is suspended in water, we can separate such a mixture either by filtration or by centrifuging. In the first case the separation takes place because liquid water is able to flow through the filter, but solid charcoal particles cannot, in the second cases the components of the mixture separate because they have different density. If iron and sulfur powders are mixed together, we can

¹i.e. the amount of heat needed to increase temperature of one kilogram of the substance one degree.

²Refractive index of transparent materials is the number that describes how fast light propagates through them.

³Refractometer is a device that measures refraction index of liquids.

⁴Quick lime, or calcium oxide, is a substance known to humans since antiquity; it is widely used for construction (masonry).

separate iron using a magnet. Not only heterogeneous mixtures are possible to separate. Sugar dissolves in water, and the resulting solution is a homogeneous substance. However, since water and sugar have different boiling temperatures the components of this solution can be easily obtained back: leave this solution in an open cup for several days, all water will evaporate, and the solid residue will be the sugar. Note, in all those examples the separation takes place due to the difference in physical properties of the components of the mixture. In other words, we separate the mixture by physical means. If some substance that can be separated onto other substances by physical means is called a mixture of substances or just a mixture, otherwise it is called a pure substance.

Preparation, characterization and study of pure substances is what majority of chemists are doing.

2 Compounds, simple substances and elements.

The fact that pure substances cannot be separated on components by physical means does not necessarily mean they cannot be separated at all. When you place a piece of sugar into a test tube and heat it, sugar melts, then its color changes to brown. If heating continues, the liquid becomes more and more dark and viscous, and finally it becomes a black solid. In addition to that, some vapors evolve that condense on the walls of the test tube to form a transparent odorless liquid. Further analysis shows that the solid formed is carbon, and the liquid is water. The same reaction made in a closed vessel yields the same products (water and carbon), which means that water and carbon are the products of decomposition of sugar, and no reaction between sugar and air takes place. However, there were no carbon and water in the piece of sugar before we started to heat it: sugar is clearly a pure substance, not a mixture. Indeed, it is impossible to obtain sugar just by mixing water with carbon. That means that, although sugar is a pure substance, it nevertheless can be converted onto other substances by chemical means (in this concrete case, decomposed at high temperature).

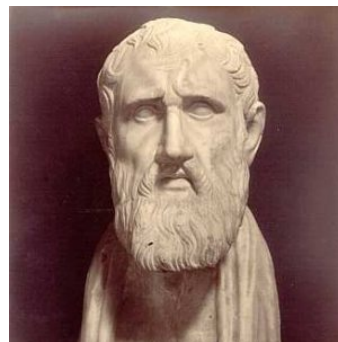
Pure chemical substances that can be decomposed on other substances are called ***complex substances***, or ***compounds***. Sugar can be decomposed, therefore it is a chemical compound (or just a compound). Since water is obtained as a result of decomposition of some compound, does that mean water is not a compound? Not necessarily. Although water is very hard to decompose, it still can be decomposed, for example by electric current. When two wires connected to positive and negative sources of voltage are immersed into water bubbles of gas start to form at their surface, and, if we continue this process long enough, all the water will disappear. What these gases are is not important now (we will talk about that later), but this experiment demonstrates that water can be decomposed on new substances, which means water is a compound, not an element. What about another product of decomposition of sugar? Numerous attempts made by early chemists to decompose it failed, so the chemists came to a conclusion that it is a substance that cannot be decomposed, i.e. a ***simple (elementary) substance***, or an ***element***. Chemical substances that cannot be decomposed onto components are called simple substances or elements. Each simple substance is composed from the atoms of a certain type. Although English literature uses the later term (“element”) almost exclusively, the two terms are not full synonyms, and many books written in French, German, Russian, etc make a distinction between them. We will

learn later why.

3 Divisibility of matter. Atoms.

3.1 Ancient Greece, geometry, philosophy and real life.

The idea that everything around us is composed of atoms seems pretty straightforward now, but is this idea really obvious? Actually, no, because nothing in our “big world” suggests the matter cannot be divisible infinitely. The first man who proposed the idea of *atoms* was a really non-trivial thinker, and the history of this concept deserves a special consideration.

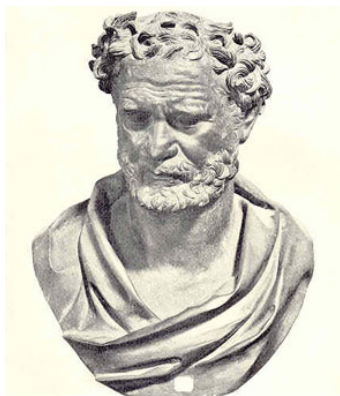


Zeno (490-430 BC)

The word “atom” (literally “indivisible”) is of Greek origin, and the Greeks came to this idea as a result of abstract considerations. Ancient Greeks were good mathematicians and brilliant philosophers (actually, they were the first philosophers).

They gave a start to abstract geometry, and, importantly, they created a concept of geometrical point, line and plane. The key idea of mathematical point is that (i) it is the object without size, and (ii) all other mathematical objects are the sets containing infinite amount of points. That means any segment of finite length can be divided onto two halves, the same can be done with the halves, and this process can be repeated infinitely. That idea looked fine in the abstract mathematical world, but an attempt to apply it to the real world lead to problems. Thus, Zeno of Elea, a Greek philosopher, concluded:

“Motion cannot exist because before that which is in motion can reach its destination, it must reach the midpoint of its course, but before it can reach the middle, it must reach the quarterpoint, but before it reaches the quarterpoint, it first must reach the eighthpoint, etc. Hence, motion can never start.”



Democritus (460-370 BC)

Since this idea, that looked logically incontrovertible, came into a clear conflict with our everyday experience, Democritus, another Greek philosopher, started to meditate about a possibility of infinite division in a real world. He concluded that would be impossible, because infinite division produces nothing, and because something cannot come from nothing. Democritus concluded that every real object can be divided only a finite number of times, and that atoms are the smallest objects everything in our world is made from. According to him, only a part of space is occupied by atoms, and the rest is void. Although the theory of Democritus helped to answer part of questions, one more step had to be made to convert it into a real chemical theory. That step was made more than two thousand years later, and we will talk about it during our next lesson.

Homework

Answer the following questions.

1. What is a substance? Explain the difference between physical bodies and chemical substances.
2. Below is a list:
"a nail, clay, a brick, a snowflake, a knife, copper wire, brass, ivory, water, wood, a plain, a metal rod, an iceberg, a segment, a tusk, sugar, salt, aspirin, mercury, the Earth, vinegar, Mercury, a Tylenol tablet, ice."
Which items in this list are (i) chemical substances; (ii) physical bodies; (iii) mathematical objects?
3. Choose some pure compound you can find in your kitchen, for example, table salt or baking soda, oil, butter, etc. Provide a detailed description of their physical properties. Describe as many properties as you can.
4. Although Democritus is considered a grandfather of atomic theory, his concept was not popular in ancient Greece or Rome, and he was essentially forgotten until XVIII century. In your opinion, why did that happen? (A hint. What is the difference between the definition of atoms given by Democritus, and the current definition?)

4 Strengths and weaknesses of the Democritus atomic theory

Although Democritus's serendipitous discovery of atomic theory laid a foundation for contemporary physics and chemistry, his theory was not popular among his contemporaries. It would be incorrect to attribute that fact to poor education or narrow-mindedness of Ancient Greek and Roman philosophers – many of them, such as Plato, Aristotle, Titus Lucretius Carus, were brilliant thinkers, who were open to logically correct arguments, and who were perfectly capable of understanding and appreciating non-trivial ideas. It would be more correct to attribute low popularity of the Democritus's idea to the internal weaknesses of the theory itself. To check that, let's look again at the main theses of the Democritus's atomic theory. It says:

1. Atoms are perfectly solid and indivisible; it is impossible to create, destroy or change them.
2. Atoms are infinite in number and various in size and shape.
3. Atoms exist in a void; they are in motion, repelling one another when they collide or combining into small or large bodies by means of tiny hooks and barbs on their surfaces, which may become entangled or detangled, depending on external conditions.

Now let's see how this theory can explain some phenomena around us.

Experiment 1

Take a piece of paraffin (for example, a piece of a candle) and put it into the glass test tube. Affix the tube in the holder and heat it gently using the gas torch or heat gun. You will see that white solid paraffin gradually melts yielding slightly turbid liquid. Now pour it onto a flat glass surface. The liquid freezes immediately giving solid paraffin.

Could Democritus explain this phenomenon based on his theory? Of course, he could. He would say: “*Obviously, in solid paraffin, the atoms hold each other tightly because of their shape. Heat breaks part of these bonds, and paraffin melts. However, when paraffin cools down all broken connections restore, and paraffin freezes back.*” That would sound quite reasonable; moreover, present-days scientists explain this process similarly, although using somewhat different terms.

Experiment 2

Take a teaspoon of table salt and dissolve it in a minimal amount of water. You may heat water gently to accelerate the process, although heating is not necessary. We see that the crystals of salt gradually disappear, and the resulting liquid remains clear, transparent and colorless. Put the liquid into a pyknometer⁵ and record its weight. Then empty the pyknometer and fill it with water. You will see that the solution of salt weighs more than the same volume of water. Now put few drops of the solution on a glass plate and heat gently using a heat gun. You will see that water evaporates, and that small white crystals form.

Again, Democritus would be perfectly able to explain these two experiments using his theory: “*The atoms of salt hold each other tightly via multiple hooks on their surface. When water is added, water atoms wedge between the atoms of salt to give a liquid which is more dense than water, because it contains a mixture of light water atoms and heavier atoms of salt. When we are heating this liquid, lighter water atoms escape, and the remaining salt atoms restore linkages between each other to form solid crystals.*” Again, this explanation is almost correct.

As we can see, the theory of Democritus is perfectly capable of explaining such phenomena as melting, crystallization, dissolution, evaporation, condensation, and similar processes. During these processes, the substances change their state, or mix together, or separate, but their chemical composition remains the same: liquid paraffin is still paraffin, and the salt dissolved in water is still table salt. These processes are called **physical processes**.

Physical processes are the processes that change the form of some substance, but not its chemical composition.

Democritus’s theory explains such phenomena quite well. Does that mean Democritus’s ideas were being rejected by Greek philosophers undeservedly? No. There are many phenomena it fails to explain.

⁵A small bottle with exactly known volume. It is used to determine density of liquids.

Experiment 3

Weigh 1.47 grams of calcium chloride dihydrate⁶, place it into a test tube or a flask, add 5 mL of water and stir gently until all solid dissolves. Weigh 1.06 grams of sodium carbonate⁷ place it into a test tube or a flask, add 10 mL of water and stir gently until full dissolution. When both liquids became clear, mix them in a conical flask or in a beaker. Describe what you observe. Using a Buchner funnel and Bunsen flask⁸ (Figure 1), filter the slurry formed, collect the solid and leave it to dry. Take few drops of the filtrate, put it on a glass plate and warm it gently using a heat gun. Describe the solid residue you obtain.

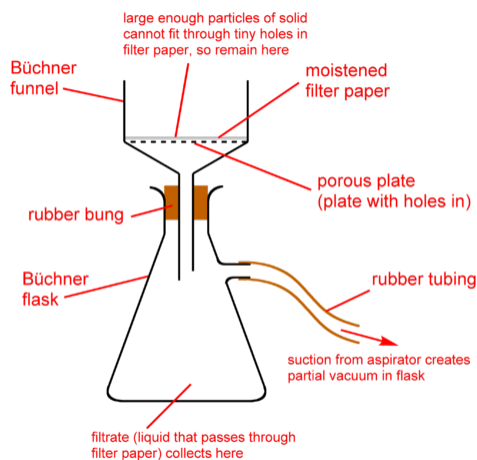


Figure 2: Vacuum filtration apparatus

The solid precipitate we obtained is a natural mineral, calcium carbonate⁹. Its properties are different from the properties of starting materials we took. Indeed, whereas both calcium chloride and sodium carbonate are soluble in water, gypsum is not, and this fact is sufficient to conclude that some new substance has been formed during our experiment. Moreover, the solid we obtained after evaporation of carbonate also is a new substance: it is ordinary table salt. We can summarize our observations by the following equation¹⁰ (1):



Had Democritus been asked to explain this process using his theory, he would have encountered a serious problem. Of course, he could be perfectly able to explain the process

⁶It is a water-soluble crystalline solid, which is being used for example as a medicine for treatment of hypocalcaemia.

⁷A.k.a. ash soda, or washing soda.

⁸Büchner funnel and Bunsen flask are the parts of laboratory apparatus used for filtration.

⁹A.k.a. chalk, limestone, marble.

¹⁰Actually, that is not exactly how chemists write chemical equations. They use chemical formulas, not words. We will learn how to draw chemical formulas a little bit later.

of dissolution of sodium carbonate or calcium chloride. However, he would be totally unable to explain the formation of sodium chloride and gypsum (as well as disappearance of sodium carbonate and calcium chloride). Remember, Democritus's atoms are impossible to create or destroy, and each substance is composed from its own type of atoms, according to him. However, if we assume some special gypsum "atoms"¹¹ do exist in nature, the question arises where these atoms have been before we started our experiment? They could be neither in sodium carbonate nor in calcium chloride, because these two are pure substances, not mixtures, and because both of them are water soluble, but calcium carbonate is not. In addition, it is not clear from the Democritus's theory why sodium carbonate or calcium chloride *alone* cannot produce gypsum, but their combination can? And, finally, one more important question remains: where sodium carbonate and calcium chloride "atoms" have gone?

We see Democritus's theory fails to explain the processes where some substances are being consumed and new substances form instead. This type processes are called **chemical reactions**.

Chemical reactions are the processes of transformation of one (or several) chemical substances to other, new substances.

Experiment 4

Place a small piece of chalk into a glass test tube and add few milliliters of dilute hydrochloric acid. You will see the bubbles of some gas will start to evolve immediately, and chalk will be dissolving gradually.

Experiment 5

Dissolve few grams of sodium carbonate¹² in 100 mL of water. Add few drops of dilute alcoholic solution of phenolphthalein¹³ to it and stir gently. The colorless solution will immediately turn pink.

The experiments 4 and 5 serve as other examples of chemical reactions. Dissolution of some material which is known to be insoluble, evolution of gas, color change - all are the traits of chemical reactions. This list is not exhaustive, moreover, sometimes the traits of a chemical reaction are hard to see (in that case chemists use special methods - we will learn about some of them later).

All these phenomena are totally impossible to explain using the original atomic theory, and that was the main reason the Democritus theory was rejected by most prominent thinkers and passed into oblivion for about two thousand years. However, it was not completely forgotten.

¹¹We use quotation marks because the actual term *atom* is not applicable here.

¹²Sodium carbonate is also called "washing soda". It can be prepared by heating ordinary baking soda in an oven

¹³Phenolphthalein is a synthetic compound that was used in past as laxative

5 From Democritus’s “atoms” to modern “molecules”



Robert Boyle (1627–91), one of the fathers of modern chemistry.

We demonstrated that the idea of indivisible and indestructible atoms as building blocks for matter was not useful for explanation of chemical reactions. The next question is, could this theory be improved or amended? Initially, philosophers didn’t believe it was possible, so the atomic theory was totally abandoned, and absolutely different concepts were proposed instead. Different candidates for the universal material were proposed by philosophers, including fire, or air, or earth, or water. Aristotle attempted to combine these ideas into a single theory: according to him, air, fire, earth, and water, when mixed in different proportions, form all other substances in our world. However, by XVII century, early chemists, such as Robert Boyle, started to learn more about properties of matter and about chemical reactions, they realized that chemical substances are probably composed of some particles of various sorts, although they avoided to call them “atoms”, and used other words, such as “corpuscula”, or “molecula”.¹⁴ The latter term be-

came more and more popular, and became commonly accepted by XIX century. In English, the word “molecula” transformed to “a molecule”.

The reason for inventing this new term (instead of an old word “atom”) was as follows. *Whereas atoms cannot be formed, changed or destroyed during chemical reactions, molecules can.* In other words, molecules have the same properties as old Democritus’s “atoms” had, except one, namely, they can be changed (actually, what he discovered were molecules, not atoms).

And what about the term “atom”? It was not fully abandoned. Chemists realized that, whereas most molecules are able to change during chemical reactions, the building blocks the molecules are composed of are unchangeable by chemical means. To name these building blocks, chemists decided to use the old name “atoms” (which was absolutely correct, because real atoms are chemically indivisible). The idea that matter is composed of atoms which are grouped in “small ultimate particles” (which we now call “molecules”) was formulated in early XIX century by British chemist John Dalton.

Dalton’s theory made a revolution in chemistry, and it lead to an explosive progress of chemical knowledge. This theory deserves a separate attention, and we will devote the next lesson to it.

¹⁴In Latin, the suffix “ula” plays a diminutive role, so “corpuscula” means “an extremely minute body” (“corpus” means “a body”), and “molecula” means “an extremely minute mass”.



John Dalton (1766–1844), the developer of modern atomic and molecular theory.

Homework

1. During this class (see **Experiment 3**), we filtered out the crystals of calcium carbonate and left them to dry. We also collected the filtrate, which contained another product of this reaction, namely, table salt. I left it to evaporate in the flask, and by the next Sunday it will be completely dry. During our next class we will weigh dry calcium carbonate and table salt we obtained today. Could you predict what the masses will be? Use the following data for your calculations. We took 1.47 grams of calcium chloride dihydrate and 1.06 grams of sodium carbonate. Assume that the masses of one molecule of starting and final compounds are as follows. Calcium chloride: 147 arbitrary units (a.u.)¹⁵, sodium carbonate: 106 a.u., calcium carbonate: 100 a.u., sodium chloride: 58.5 a.u. *Please keep in mind that in this reaction one molecule of calcium chloride reacts with one molecule of sodium carbonate yielding one molecule of calcium carbonate and two molecules of salt.* You need to take that fact into account in your calculations. I believe you were able to solve the first problem easily (it is not as formidable as seems). However, to solve this problem you had to make some implicit assumptions. Try to formulate them explicitly. Which law can be derived from our experiment?

As usually, I would be grateful if you sent me your homework by evening of next Saturday. My e-mail is mark.lukin@gmail.com

¹⁵So far, we do not care what does a.u. mean. We can perfectly do all computations without knowing what one a.u. is equal to.