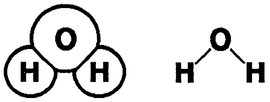
Chapter 3

CHEMICAL UNITS AND THEIR IDENTITIES, Part 2

Now we get into the nit and the grit of compounds.

As we've seen, a compound is composed of atoms of two or more elements chemically bonded within some chemical unit. Water is a very common example. As mentioned in the last Chapter, water involves molecules which have two hydrogen atoms and one oxygen atom. The formula is H_2O. The atoms are not in a straight line; instead they form a bend. Why? It's because the electrons require it to be this way. You'll see, beginning in Chapter 28, how to predict shapes based on electrons.



Compounds are their own chemical identity. The chemical units of compounds have their own <u>specific number of specific atoms in a specific arrangement</u>. Each different compound will have its own set of physical and chemical properties. The properties of water have no similarity at all to the properties of elemental hydrogen or elemental oxygen. The electrons are arranged in a certain way in a water (H_2O) molecule. The electrons are arranged in a certain way in a hydrogen (H_2) molecule. The electrons are arranged in a certain way in an oxygen (O_2) molecule. Because all of these arrangements are totally different, the properties are totally different.

There are over 100,000,000 known compounds, and there's really no limit to how many more can exist. We commonly classify compounds by the types of chemical bonds which hold their atoms together. There are three very general types of chemical bonds: ionic, covalent and metallic. We'll talk a lot about them in much later Chapters. For now we just need a brief introduction so that we can use the terms to distinguish compound types. We won't do much with metallic right now. As the name indicates, this type of bond occurs in the elemental forms of metals and in metal alloys, and that's all we need to know for now. Our major emphasis here will be ionic and covalent types.

3.1 Ions and ionic compounds

An ionic compound is one which is composed of "ions". An ion is a monatomic or polyatomic chemical unit with a charge. In the last Chapter, I said a neutral atom has no charge because the number of protons and the number of electrons is the same and the charges cancel each other. But I also said that not everything is neutral. This brings us to ions. In ions, the number of electrons and the number of protons are different, which means there's a charge on the unit.

Ions come in two general types. Cations have <u>less electrons than protons</u>. This means less negatives than positives, so not all positives cancel. That leaves the cation with a net positive charge. The converse is the anion. Anions have <u>more electrons than protons</u>. This means more negatives than positives, so not all negatives cancel. That leaves the anion with a net negative charge. Cations positive. Anions negative. Remember that.

Due to the way their electrons are arranged, many atoms have a tendency to form monatomic ions. For example, all natural compounds of sodium on Earth involve ionic compounds in which the sodium is actually a sodium cation. A sodium <u>atom</u> would have 11 p^+ and 11 e^- and would be neutral, but a sodium <u>cation</u> has 11 p^+ and only 10 e^-. (Neutrons don't matter here since they have no charge. So we're ignoring them. Yes, they're still in there.) Since there's one less e^- than there are p^+'s, the ion has a charge of 1+. We represent the ion by the formula Na^+, with the charge as a superscript after the element symbol. Let's do an ion of fluorine. A neutral fluorine <u>atom</u> has 9 p^+ and 9 e^- but the <u>ion</u> has 9 p^+ and 10 e^-. Since it has one more e^- than p^+'s, the ion has a charge of 1–. We represent the ion by the formula F^-.

Ion charges are not limited to 1+ or 1–. They can be 2+ or 2– or 3+ or 3–, etc. More examples include O^{2-} or Mg^{2+} or Al^{3+} or N^{3-}. Higher charges than 3+ or 3– are iffy and there are restrictions with going higher. Why? It costs energy and the higher charges are too expensive in most cases. You can see more of this in Chapter 23 and later Chapters.

Notice from the example of Na^+ and of F^- that, when the charges are 1+ or 1–, then the ones are not included in the superscript. Other charges must show <u>sign and number</u> in the superscript, like O^{2-}, Mg^{2+}, Al^{3+} and N^{3-}. Also notice that, in the charge superscript, <u>the charge number is before the sign</u>.

An ion is its own chemical unit and has its own identity. Ions don't just exist by themselves, however, under normal conditions. For conditions on Earth, <u>Nature requires neutrality</u>. (In space, conditions are different and ions can exist by themselves. Not only that, the charges can be very large since the energies are out of this world. But we're not doing the whole cosmos here.) Every ionic compound has BOTH cations and anions in a ratio which makes the ionic compound neutral overall. This ionic compound also has its own identity. For right now, we are going to focus on separate ions; later, we'll do whole ionic compounds. The point I need to make right now is that there are two levels of chemical units and of identities when dealing with ionic compounds. You have the chemical units and identities of the cations and anions separately. After that, when a specific cation and a specific anion combine to make an ionic compound, then you have the chemical unit and the identity of that compound. Compounds come later; we do separate ions now.

There are two things you MUST remember as we go. First, ION CHARGES ARE DUE TO VARIATIONS IN THE NUMBER OF ELECTRONS ONLY. The number of protons and neutrons stays the same. This is another example that electrons do chemistry. Second, FORMULAS FOR IONS MUST INCLUDE THE CHARGE. Always, always, always. Some students get a little lazy (or forgetful) and don't write the charge when they write the symbol for an ion. For example, if asked to write the symbol for the sodium ion, they write Na instead of Na^+. That's just asking to lose points on exams. (I told you this was also a survival guide. Read and heed.)

Some elements can form different ions with different charges. Iron is good at this: some iron ions are Fe^{2+} (24 e^-) and some are Fe^{3+} (23 e^-). Other ions, however, are locked into the same charge all the time. Calcium ions will only be Ca^{2+}. We distinguish these cases as "variable charge ions" and "constant charge ions". "Variable charge" applies for elements (such as Fe) which can form ions of different charges in their different, common ionic compounds. "Constant charge" involves those elements (such as Ca) which will always form the same ion of the same charge in their common ionic compounds. Ca^{2+} and numerous examples above (Na^+, F^-, O^{2-}, Mg^{2+}, Al^{3+} and N^{3-}) are constant charge cases. You won't find an ionic compound with a Na^{2+} cation. You won't find an ionic compound with a F^{2-} anion. Et cetera. Iron ions are variable charge examples. In fact, most (not all) of the transition elements and inner transition elements are in this category. Notice that IONS OF THE SAME ELEMENT BUT DIFFERENT CHARGES ARE DIFFERENT CHEMICAL UNITS AND HAVE DIFFERENT IDENTITIES. Fe^{2+} and Fe^{3+} ions are different. They have different numbers of electrons. They do different chemistry.

Why do ions of some elements form the same charge all the time and others can form different charges? Why are some ions 1+ while others are 2– while others are 3+ or whatever? It's in the electron arrangements. It depends on how many electrons are in the atom, where they are in the atom and what are their energies. Again, greater details and explanation can be found in later Chapters. We don't need that right now because we are more concerned with what are the charges. We can do why later. We already have a tool to help us with what are the charges: it's the Periodic Table. Remember in the last Chapter that I said the Periodic Table is related to electron arrangements. I just now said that charges are also related to electron arrangements. Put the two together and you realize that charges and the Periodic Table are related. You can use the Periodic Table as a guide for what charges a particular element typically will adopt in its monatomic ions. These are guidelines, not rules. They're good but not perfect. There will be exceptions. Your instructor may use a different set of guidelines.

Our guidelines for monatomic ions are based on four categories. Flag this part for later reference: put "ion charges" in the margin.

- CATEGORY 1. CONSTANT CHARGE CATIONS

  A. Metal elements of Groups 1, 2 and 13 form cations of charge 1+, 2+, and 3+, respectively.

  We've already considered several examples including Na^+ (Na is in Group 1), Mg^{2+} (Mg is in Group 2) and Al^{3+} (Al is in Group 13).

  B. Zn forms Zn^{2+} and Ag forms Ag^+.

  These two are transition elements. Most of the transition elements are variable charge cases, but these two are usually constant charge. They are also very commonly encountered so we set them aside here.

- CATEGORY 2. VARIABLE CHARGE CATIONS

  Most other metal elements form cations but their charges can vary depending on the type of compound at hand.

  The charges cannot be predicted readily unless a specific compound is given or other information is given. Most of the transition elements are in this category but there are also a few Main Group elements (such as tin and lead) which are also here.

- CATEGORY 3. CONSTANT CHARGE ANIONS

  The nonmetal and metalloid elements commonly form anions in which the charge is equal to the Group number minus eighteen.

  All of our anion examples from above fall in this Category: F^- (F is in Group 17, so 17 – 18 = –1), O^{2-} (O is in Group 16, so 16 – 18 = –2) and N^{3-} (N is in Group 15, so 15 – 18 = –3). Why the number 18? It's related to the total number of Groups, but both of these are related to how electrons are arranged in atoms and ions. Again, we shall see this in later Chapters.

- CATEGORY 4. HYDROGEN

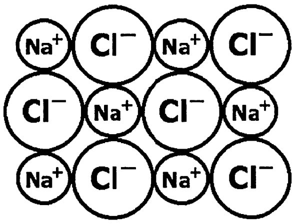
  Hydrogen can form H^+ or H^- depending on the circumstances.

  This is a very limited case and very few other elements commonly do this. Ironically, there are no compounds with the H^+ ion on Earth, but this ion is hugely abundant in space. On the other hand, there are various compounds with H^-.

There are two points to note for these categories. First, notice that Categories 1 and 2 refer to metal elements while Category 3 involves otherwise. This is a useful application of PoBiSnAl for distinguishing metal elements from elements which are not metals. Second, these are guidelines. There are going to be exceptions. We will expand on this later in Chapter 25. For now, if you see something that doesn't fit, don't worry about it. The guidelines are meant as a predictive tool. It remains your job to accept that exceptions can happen, even if you would not be responsible to predict them at this stage of the game.

Alright, this concludes our introduction to monatomic ions. There are also polyatomic ions but I can't do them yet. We have to get through the next section first.

As mentioned earlier, ions make up an ionic compound and an ionic compound has ionic bonds. Every ionic compound must be neutral overall, so the cations and anions must be in the right ratio to cancel each other's charge. We'll do ratios later. Let's briefly describe ionic bonding. It's very straightforward.



Ionic bonding is simply the +/– attraction between cations and anions. Pluses like minuses and vice versa, so cations and anions naturally want to get together. That's ionic bonding. The bonding extends in all three dimensions throughout the sample. Each cation is next to or near anions and each anion is next to or near cations. Here is a partial drawing using Na^+ and Cl^- ions as an example. (By the way, that's your table salt.) In an ionic solid, the arrangement is cation-anion-cation-anion-cation-anion-cation-anion, etc-etc-etc. This arrangement goes in three dimensions, even though I only drew it as 2D. The bonds extend for zillions and zillions of ions. Because of this, ionic compounds are another type of "network compound"; specifically, these are ionic networks.

There's a subtlety in the picture here which I would like to point out, compared to our F_2 molecule from Chapter 2. In Chapter 2, I said that the atoms in F_2 overlapped. Now, for ions, I draw Na^+ and Cl^- ions as touching, but not overlapping. In a true ionic picture, overlap is not significant. There are technicalities with this, some of which are described in Chapter 25, but we don't need those right now. We are yet in the very early stages of the Grand Puzzle.

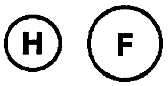
Before leaving ionic compounds, I want to remind you of something I said above about identity and how there are two levels of identity for an ionic compound. Every ion by itself is a chemical unit and has its own identity. Ionic compounds exist for widely diverse combinations of cations and anions. When you have a specific cation combined with a specific anion, then that is a specific ionic compound with its own identity and its own properties. Table salt with Na^+ cations and Cl^- anions is not the same as the compound with K^+ cations and Cl^- anions. Although the anion is the same, the compounds are different. They even taste different. The K^+/Cl^- combination is used as a salt substitute and you can buy it in the grocery store. It's useful for people who are trying to limit sodium intake.

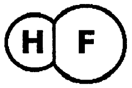
OK. Enough for ionics temporarily. Let's go covalent.

3.2 Covalent compounds

Before doing a covalent compound, we first bring in our second bond type: the covalent bond. The covalent bond is a chemical bond which involves sharing electrons. Each atom of the bond shares electrons with the other atom of the bond. It is this mutual sharing which holds the atoms together in the bond.

Let's illustrate a simple case with the diatomic molecule, HF. If we consider the atoms separately as shown at right, we have one H with one electron and one F with nine electrons. The F atom is bigger than the H atom for reasons to be seen in Chapter 23.





In the HF molecule, the two atoms are overlapped. I show this at left. Now, I want to tell you why overlap is so important.

When two atoms overlap their electrons, then some electrons actually become shared between the two atoms. For the molecule HF, two electrons are shared over both atoms. The H contributes its one electron to the share and the F contributes one of its nine to the share. The two shared electrons surround the entire molecule and this holds the atoms together. This is the covalent bond. The volume occupied by all electrons combined now defines the size of the molecule, as shown at right.

There's a lot more to explaining how a covalent bond works, much more than we want right now. We'll just keep it as sharing for the time being. In our HF molecule, the share involves two electrons but the number of electrons shared in other covalent bonds can vary up to twelve. By far, the most common numbers of shared electrons are two, four and six. Here's another feature: the share can actually occur over three or more atoms. How do you tell how many electrons are shared over how many atoms? Don't worry about that right now. We'll do that later, starting in Chapter 25, when we venture into more details of the covalent bond.

One of the biggest points of emphasis for now is that <u>every individual neutral molecule uses covalent bonds to hold its atoms together</u>. This includes the molecules we talked about in Chapter 2 for elemental forms such as F_2, H_2, O_2, O_3, P_4, S_8, etc. Some network elemental forms also involve covalent bonds; diamond and graphite are examples. Covalent bonding can also occur in compounds, which brings us to the term "covalent compound". A covalent compound is one which uses only covalent bonding. Good old water, H_2O, is a premier example. HF is another covalent compound. So also are table sugar ("sucrose", $C_{12}H_{22}O_{11}$), quartz (SiO_2), carbon dioxide (CO_2), etc. ALL COVALENT COMPOUNDS ARE COMPRISED OF MOLECULES OR THEY ARE NETWORKS. <u>There are no ions whatsoever.</u> H_2O, HF, $C_{12}H_{22}O_{11}$ and CO_2 are all composed of individual molecules. Quartz, SiO_2, is a covalent network compound.

I mentioned table sugar. Actually the word "sugar" in chemistry represents an entire family of compounds. Common table sugar (sucrose, also called cane sugar) is only one example. Nature uses many different sugars in many different organisms. Fruit sugar is fructose. Blood sugar is glucose. Milk sugar is lactose. Why am I bringing this up? It's because I want to point out something else about chemical units and identity. Remember that each has its own specific number of specific atoms in a specific arrangement. If you change any of the three you change the chemical unit. Fructose is $C_6H_{12}O_6$. Glucose is $C_6H_{12}O_6$. They have the same formulas because they have the same number of the same atoms in their molecules. But they have different arrangements for these atoms in their molecules. So, although they have the same number of the same atoms, they are still different compounds with different physical and chemical properties. These are called "isomers". Isomers are different chemical units with the same formula but with different arrangements of their atoms. Nature is extremely prolific at utilizing different isomers in different ways. Even sucrose and lactose are isomers; they're both $C_{12}H_{22}O_{11}$.

Alright, enough of the sweet talk.

Three paragraphs ago, I said a covalent compound is one which uses <u>only</u> covalent bonding. This wording is very specific. Some compounds can use covalent AND ionic bonding. These are not considered covalent compounds. They are considered ionic compounds. That's where we go next.

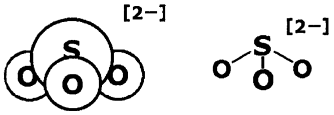
3.3 What to do about polyatomic ions

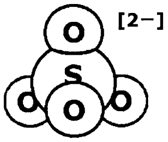
Compounds which use both covalent and ionic bonding involve a polyatomic ion. I made brief mention of them earlier but I had to delay them for a page or so. Here we are.

I first defined an ion as a monatomic or polyatomic chemical unit with a charge. Polyatomic units can have charges for the same reason a monatomic can have a charge: the <u>total</u> numbers of electrons and of protons in the chemical unit are different. "Sulfite" is the name of the polyatomic ion, SO_3^{2-}. It has one sulfur atom (which owns 16 p^+) and three oxygen atoms (which own 8 p^+ each, for a total of 24).

The whole sulfite ion has a total of 40 p^+ in the four nuclei of the chemical unit. The ion has a total of 42 e^-, however, thus giving two more electrons than the total number of protons. That's why it's an ion and that's why its charge is 2−.

Sulfite ions are somewhat common. Sulfite compounds are used as food preservatives in a number of grocery items. They are somewhat toxic to humans in general and the amounts used in foods are kept below the generally hazardous amounts. Unfortunately, some people are born with an extreme sensitivity to sulfite compounds; they have to be very careful in grocery stores and restaurants regarding which foods they buy and eat. These individuals are said to be "sulfite sensitive"; for them, even a very small amount of sulfite can be fatal.

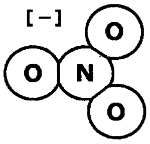


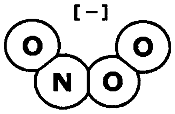


The sulfite ion has a pyramid shape with S at the top, as shown at right. The O's are bonded to the S by covalent bonds. Every polyatomic ion uses covalent bonds between the atoms which make up that ion. Since a polyatomic ion is a chemical unit, each polyatomic ion has a specific number of specific atoms in a specific arrangement. A key difference when compared to molecules is that a polyatomic ion also carries a specific charge. All of these together give the identity of the polyatomic ion. Change one part and you change identity. Sulfite, SO_3^{2-}, above, is toxic. Increase the number of oxygen atoms by one and you get sulfate, SO_4^{2-}, at left, which is fairly harmless. These are critical distinctions. They matter in a very big way.

Let's spell this out again for emphasis: the identity of a polyatomic ion is given by a specific number of specific atoms in a specific arrangement and with a specific charge overall. If you change any one of those four criteria, then you change the identity of that ion.

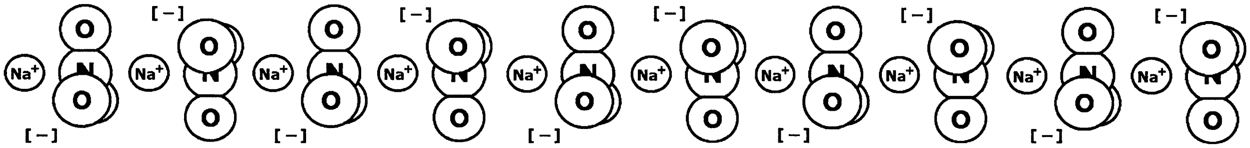
Polyatomic ions can also do isomers. These will have the same number of the same atoms and they will have the same charge, but they have a different arrangement of the atoms. Nitrate, NO_3^-, at left, is fairly harmless in very small amounts and it is useful as a fertilizer. Peroxynitrite, NO_3^-, at right, is potently harmful and attacks various components in your cells. Although these two ions have the same number of the same atoms and the same charge, the atoms are in different arrangements; therefore, these are different chemical units.





As we describe various ions, you must remember that one ion by itself does not make a compound. As I said before, ions don't just exist by themselves at typical Earth conditions. Nature requires neutrality. Every ionic compound has BOTH cations and anions in a ratio which makes the ionic compound neutral.

Let's consider an ionic compound which has a polyatomic ion. We'll show a compound with the nitrate anion, NO_3^- (above at left), combined with a sodium cation, Na^+. Just as in the ionic compounds earlier, there are cations and there are anions and these are bonded to each other by ionic bonding extending in three dimensions: cation-anion-cation-anion-cation-anion-cation-anion, etc-etc-etc., all held by ionic bonding. I've got one row drawn here for simplicity, but three dimensions are really involved.



The nitrate ion is flat, but I flipped it on its edge in order to properly convey this line-up. I also left some space between the ions so that you can see them better. Although the polyatomic anion has covalent bonds within it, the compound itself is classified as an ionic compound, not as a covalent compound. Ionic compounds will always have ionic bonds but they may also have covalent bonds if a polyatomic ion is involved. Covalent compounds will only have covalent bonding.

There is a huge number of different polyatomic ions. It will become important for you to recognize a given formula as a polyatomic ion. This is not necessarily straightforward by itself and it will require some memorization. Instructors typically provide their students with a list of polyatomic ions to know. Their names and formulas are important to the language of chemistry just like the names and formulas of compounds. We'll get to this in the next Chapter.

Be sure to remember that a polyatomic ion is a chemical unit with its own identity. It stays together unless there is a chemical change (reaction). An occasional mistake by students is to think that the polyatomic ion is composed of monatomic ions by itself. Some think SO_3^{2-} is composed of the ions S^{2-} and O^{2-}. This is wrong. On an exam, it's really wrong.

3.4 Wrap up

Chapters 2 and 3 lay down a lot of groundwork for many things to come, in the short term and in the long term. There are numerous, very important concepts and terms involved. This would be a good time to summarize some of that.

- Regarding elemental forms and compounds in general: some are monatomic, some are molecular and some are networks. Here are a few key features.
  - Group 18 elemental forms are monatomic.
  - Everything else is polyatomic, which includes molecular substances and network substances.
    - Ionic compounds are networks.
    - Metal elemental forms are networks.
    - Covalent substances include many elemental forms and many compounds. Some of these are networks and some are molecules.
- We have also distinguished two different bond types and two different compound types.
  - Bond types
    - Ionic bonds result from the +/− charge attraction between cations and anions.
    - Covalent bonds result from sharing electrons among two or more atoms. This occurs within molecules and within every polyatomic ion.
  - Compound types
    - Ionic compounds have cations and anions which are bonded together by ionic bonding. The cation and/or anion can be monatomic or polyatomic.
    - Covalent compounds involve only covalent bonds. No ions and no charges are involved.

I will now note that metal elemental forms use metallic bonding, but we won't deal much with that type of bonding until Chapter 33.

Problems

1. True or false.
   a. Barium forms constant charge cations of 3+ charge.
   b. Cu^+ and Cu^{2+} are different ions and have different properties.
   c. CO and CO_2 are isomers.
   d. Polyatomic ions contain covalent bonds.
   e. Ionic compounds are network compounds.

2. a. What is the formula of the monatomic ion which has 23 protons and 20 electrons?
   b. What is the formula of the monatomic ion which has 15 protons and 18 electrons?
   c. What is the formula of the monatomic ion which has 31 protons and 28 electrons?

3. a. How many electrons are in one Co^{3+} ion?
   b. How many electrons are in one Nb^{2+} ion?
   c. How many electrons are in one Br^- ion?

4. a. What is the symbol for the element which forms a 2− monatomic anion containing 54 electrons?
   b. What is the symbol for the element which forms a 2+ monatomic cation containing 44 electrons?
   c. What is the symbol for the element which forms a 1+ monatomic cation containing 36 electrons?