The Basics of Water Chemistry (Part 1)

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Summary: Water chemistry is basic but, nonetheless, it’s still chemistry. Some people shy away from trying to understand his subject because they feel it’s over their heads. However, understanding the fundamentals of chemistry is necessary in order to grasp the full breadth of how certain aspects of water filtration work—especially ion exchange.

Part 1 of this article will point out the basic ionization process and the relationships that exist between one species and another. It will also introduce the reader to the wealth of information available on the Periodic Table of Elements, the universal guide to chemical properties. Part 2 will examine the guidelines for the proper use of a water analysis and point out some traps to avoid. Part 3 will then describe how to use chemistry and ion exchange selectivity to solve certain treatment problems.

Mother Nature keeps an orderly house. There are less than 100 elements “in nature” and, by definition, they’re all separate and distinct from one another. Copper, nickel, tin, zinc, sodium and oxygen are all elements.

Elements are made up of a balanced number of positive and negatively charged particles called protons (+) and electrons (-), which, along with neutrons (which are neutral), form an atom of that element. The atom is the smallest particle still identifiable as having the properties of the element. All elements are, being balanced with the same number of electrons and protons, neutral in charge.

All elements can—and do—have different numbers of protons with a matching number of electrons. Hydrgen (H) has only one whereas Helium (He) has two. Lithium (Li) has three and so on all the way up to Uranium (U), which has 92. Plutonium (Pu), a manmade element that doesn’t exist in nature, has 94 electrons and protons. The heaviest element known, Unihexium (Unh), also manmade, has 106. So, all numbers from 1 to 106 are accounted for. Each differs by only one proton and each is a totally separate substance with its own unique properties.

We use the term Atomic Number (AN) to identify each of the elements and this number corresponds to the number of electrons of the element. These various elements are conveniently arranged on a chart we refer to as the Periodic Table of Elements (see Figure 1). The periodic table contains a wealth of information such as density, melting point, boiling point as well as valence, atomic weight and atomic number. Elements are grouped in “families” which have similarities and predictability of reaction.

Atomic weight (AW) represents the mass of an element and is the total of its protons and neutrons. It is possible to have elements of differing atomic weight, but with the same atomic number because the number of neutrons can vary. We refer to these variations as isotopes. For example, chlorine, which is element 17, can have 18 or 19 neutrons. Therefore, it has an atomic weight of 35 or 36. Since these two common isotopes exist in nearly the same percentage, we assign chlorine an atomic weight of 35.5.

The jagged line drawn through the chart in Figure 1 separates the metals from the non-metals (on the right). This helps you to determine how that substance will react with oxygen and subsequently, how that compound will react with water. You might have noticed that boron (B), carbon (C), nitrogen (N), fluorine (F), silica (Si), phosphorous (P), sulfur (S), chlorine (Cl), arsenic (As), etc., on the non-metal side all seem to end up on the same side of the salt molecule. In other words, they are the acid formers whereas hydrogen, sodium, calcium, etc., are the base formers.

When subjected to heat in the presence of oxygen, most metals will form a metal oxide. The most common observation of this is rust, which is iron oxide. Lime is calcium oxide (CaO) and caustic (Na_2O) is sodium oxide. If we subscribe to the theory of a fiery creation, we can readily see where the heat came from. When a metal oxide is dissolved into water, a basic, or alkaline, solution is created, as can be seen in Reaction 1 in Figure 3. Non-metals, such as sulfur (S) and nitrogen (N) also form oxides, but when dissolved into water, they form acids. (See Reaction 2 in Figure 3.)

When elements combine to form compounds, nature preserves the laws of neutrality. Ammonia (NH_3) is a gaseous compound made up of one atom of nitrogen and three atoms of hydrogen. Sodium chloride (NaCl) is a compound that's a salt. What determines how many of this will react with how many of that to form so many of those also is fixed by the nature of the element.

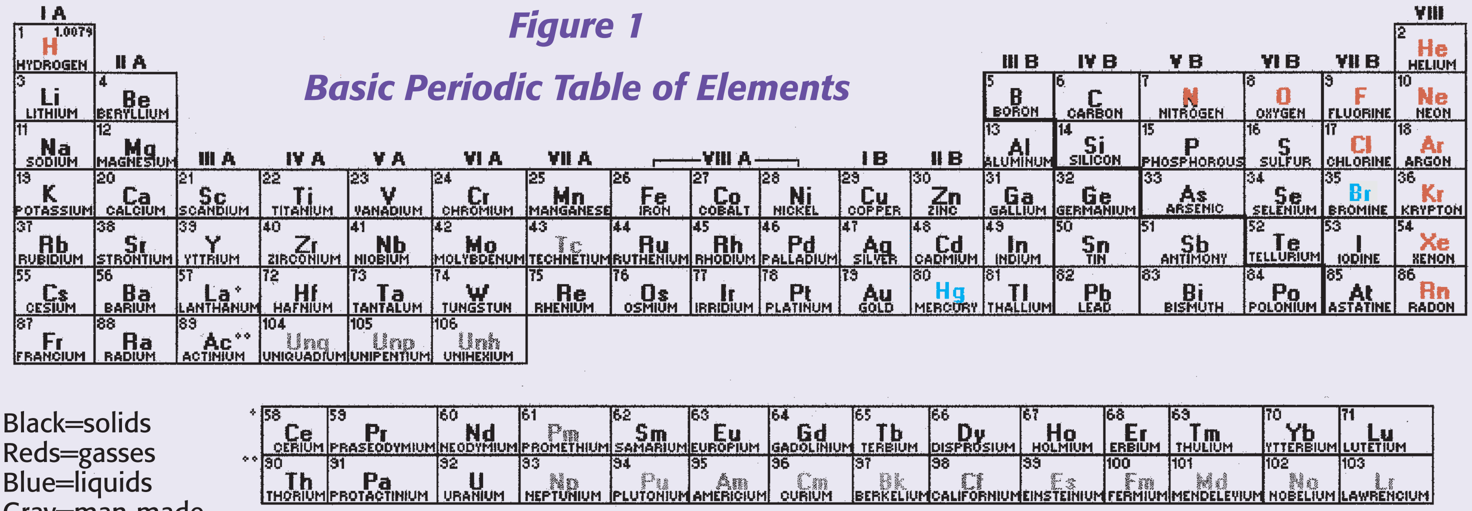


Figure 1
Basic Periodic Table of Elements

I A	II A	III A	IV A	V A	VI A	VII A	VIII A			I B	II B	III B	IV B	V B	VI B	VII B	VIII
1 1.0079 H HYDROGEN																	2 He HELIUM
3 Li LITHIUM	4 Be BERYLLIUM											5 B BORON	6 C CARBON	7 N NITROGEN	8 O OXYGEN	9 F FLUORINE	10 Ne NEON
11 Na SODIUM	12 Mg MAGNESIUM											13 Al ALUMINUM	14 Si SILICON	15 P PHOSPHOROUS	16 S SULFUR	17 Cl CHLORINE	18 Ar ARGON
19 K POTASSIUM	20 Ca CALCIUM	21 Sc SCANDIUM	22 Ti TITANIUM	23 V VANADIUM	24 Cr CHROMIUM	25 Mn MANGANESE	26 Fe IRON	27 Co COBALT	28 Ni NICKEL	29 Cu COPPER	30 Zn ZINC	31 Ga GALLIUM	32 Ge GERMANIUM	33 As ARSENIC	34 Se SELENIUM	35 Br BROMINE	36 Kr KRYPTON
37 Rb RUBIDIUM	38 Sr STRONTIUM	39 Y YTTRIUM	40 Zr ZIRCONIUM	41 Nb NIOBIUM	42 Mo MOLYBDENUM	43 Tc TECHNETIUM	44 Ru RUTHENIUM	45 Rh RHODIUM	46 Pd PALLADIUM	47 Ag SILVER	48 Cd CADMIUM	49 In INDIUM	50 Sn TIN	51 Sb ANTIMONY	52 Te TELLURIUM	53 I IODINE	54 Xe XENON
55 Cs CESIUM	56 Ba BARIUM	57 La* LANTHANUM	72 Hf HAFNIUM	73 Ta TANTALUM	74 W TUNGSTUN	75 Re RHENIUM	76 Os OSMIUM	77 Ir IRRIDIUM	78 Pt PLATINUM	79 Au GOLD	80 Hg MERCURY	81 Tl THALLIUM	82 Pb LEAD	83 Bi BISMUTH	84 Po POLONIUM	85 At ASTATINE	86 Rn RADON
87 Fr FRANCIUM	88 Ra RADIUM	89 Ac** ACTINIUM	104 Unq UNIQUADIUM	105 Unp UNIPENTIUM	106 Unh UNIHEXIUM												

*	58 Ce CERIUM	59 Pr PRASEODYMIUM	60 Nd NEODYMIUM	61 Pm PROMETHIUM	62 Sm SAMARIUM	63 Eu EUROPIUM	64 Gd GADOLINIUM	65 Tb TERBIUM	66 Dy DISPROSIUM	67 Ho HOLMIUM	68 Er ERBIUM	69 Tm THULIUM	70 Yb YTTERBIUM	71 Lu LUTETIUM
**	90 Th THORIUM	91 Pa PROTACTINIUM	92 U URANIUM	93 Np NEPTUNIUM	94 Pu PLUTONIUM	95 Am AMERICIUM	96 Cm CURIUM	97 Bk BERKELIUM	98 Cf CALIFORNIUM	99 Es EINSTEINIUM	100 Fm FERMIUM	101 Md MENDELEVIUM	102 No NOBELIUM	103 Lr LAWRENCIUM

Black=solids
Reds=gasses
Blue=liquids
Gray=man-made

The importance of orbits

The electrons contained in each of the elements are arranged in electron orbits around the shell of the atom's nucleus (center). There is more than one orbit—in fact, there are many. However, each orbit is filled with only a certain number of electrons and that number is more or less the same for all of the elements. Since the number of electrons differs by only one from one element to the next on the periodic chart, only the outermost orbit will contain a different number of electrons. This tiny difference determines many of the properties of that element and the family to which it belongs. For instance, hydrogen, lithium, sodium and potassium all have only one electron in their outermost orbit. Magnesium, calcium and strontium each have two. Fluorine, chlorine, bromine and iodine—the halogen family—each have seven. On the far right of the Periodic Table, helium, neon, argon, krypton, xenon and radon form the inert gasses (non-reactive). Are we starting to get the picture of just how valuable the periodic table might be?

When electrons react to form compounds, they tend to go to a less reactive state. In other words, they try to imitate the "relaxed" state of the inert gases by filling their outer orbits to completion. The innermost orbit needs only two electrons (or zero). The outermost generally wants eight. We can see from the periodic table that hydrogen, AN=1, has only one electron in its outer orbit. Oxygen with an AN=8 has two in its inner and six in the outer. To be “satisfied,” hydrogen will give up its electron and oxygen will pick it up. However, to satisfy the full demand of the oxygen, it will require two hydrogens to make the supreme sacrifice—thus, forming the basis of water. This is shown in Reaction 4 in Figure 3 as well as graphically with a depiction of the electron exchanged in Figure 2.

Table 1

Common Elements Found in Tap Water

Element	Ionic Form	Valence
Calcium	Ca^{++}	+2
Magnesium	Mg^{++}	+2
Sodium	Na^{+}	+1
Potassium	K^{+}	+1
Aluminum	Al^{+++}	+3
Iron	Fe^{++}	+2 (ferrous)
	Fe_2O_3	0 (ferric, rust)
Manganese	Mn^{++}	+2 (manganous)
Fluoride	F^{-}	-1
Chloride	Cl^{-}	-1
	OCl^{-}	-1 (free chlorine)
Oxygen	OH^{-}	-1 (hydroxyl)
Nitrogen	NO_3^{-}	-1 (nitrate)
	NO_2^{-}	-1 (nitrite)
	NH_4^{+}	+1 (ammonia)
Sulfur	$SO_4^{=}$	-2 (sulfate)
	$SO_3^{=}$	-2 (sulfite)
	$S^{=}$	-2 (sulfide)
Carbon	HCO_3^{-}	-1 (bicarbonate)
	$CO_3^{=}$	-2 (carbonate)
Silica	SiO_2	0 (colloidal)
	H_2SiO_3	<-1(weakly charged acid)

Other than the inert gases, all elements will have from one to seven electrons in their outer orbits. They can either give them up or pick up additional ones to satisfy a full orbit. Sodium, which has one, will give that up to chlorine, which has seven. Thus both the chlorine and the sodium are satisfied and the resulting compound, NaCl, is neutral. Potassium has one and oxygen has six. Therefore, oxygen needs two and the resulting compound of potassium oxide is balanced as K_2O.

The role of salt and water in ion exchange

When salt is dissolved in water, the two components of the salt separate. However, they don’t regain their original electron counts and therefore are no longer neutral. Since they now have either gained or lost electrons (which have a negative charge), they’ll have either a net positive (loss of electrons) or net negative (gain of electrons) charge. We call these charged particles ions. The positive ion is called a cation and a negative ion is called an anion. The number of electrons gained or lost by the element determines the strength of the charge. We call this charge its valence and we denote this by writing the symbol for the element or compound with a corresponding number to signify its ionic charge. Thus, sodium is Na and its ion is Na+. Chlorine is Cl and its ion is Cl-.

Table 1 lists some of the more common elements found in tap water, the compound form most likely and its valence.

In general, all metals—even gold—will form oxides and, therefore, bases; Most non-metals will form acids. Acids neutralize bases to form salt and water. This is the most fundamental reaction in chemistry and perhaps, the most important one for ion exchange function. This reaction is shown in Reaction 3 in Figure 3.

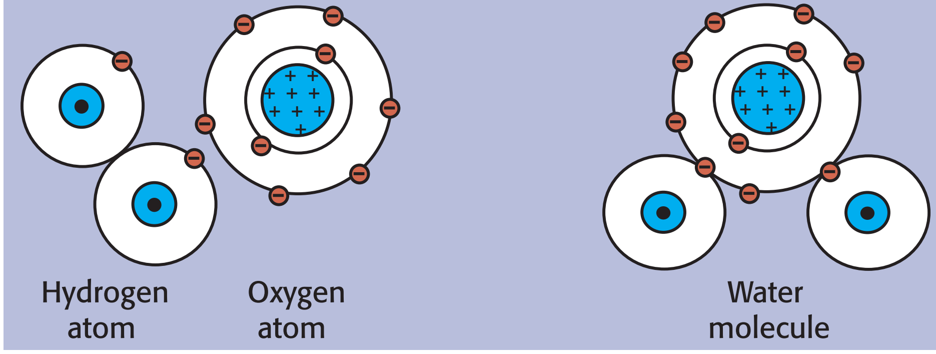
Water, H_2O, does not ionize as H+ and O=. Instead, it becomes H+ and OH-. We call the OH ion a hydroxyl ion and denote it with a negative one charge. These two ions are the backbone of the ion exchange demineralizer reaction, which is very simply a commercial application of the most basic law of chemistry shown, again, in Reaction 3 in Figure 3.

Although we commonly refer to sodium chloride (NaCl) as “salt”—which it is—it’s not the only salt. Any product of neutralization between an acid and a base will form a salt. Magnesium sulfate is a salt; potassium citrate is a salt. The names of salts usually have “-ide,” “-ite” and “-ate” endings.

Selectivity

If we add two different soluble salts to water, say sodium carbonate and calcium chloride, we produce four different ions: Ca++ (calcium), Na+ (sodium), Cl- (chloride) and CO_3= (carbonate). The fact that the Ca++ and CO_3= are more strongly charged is a hint that they're more strongly attracted to one another. Being more strongly attracted means decreased solubility. Indeed, if we add enough Na_2CO_3 (soda ash) to $CaCl_2$, we do precipitate $CaCO_3$, leaving a solution of salt (NaCl) and perhaps some excess Na_2CO_3 and a slight amount of soluble $CaCO_3$.

Figure 2
How water is formed selectively



This process has been used for effectively softening water (removing excess hardness). We see in this example that the ions exchange partners (hence the name, ion exchange) in order of attraction and ionic strength. This is known as ion selectivity and is the backbone of the ion exchange process.

As shown by Reaction 5 in Figure 3, certain elements or compounds in water can be made to undergo specific selective reactions and these reactions are predictable to some degree according to the element's family association in the periodic table. Divalent ions (those with a double positive charge) such as calcium and magnesium, will react with soap and cause "bathtub ring." They also will react with the carbonate ion to form scale in pipes and heaters. Although we could precipitate these salts with the addition of carbonate ions (see Reaction 5 in Figure 3), we have no easy way to remove the resulting solid. Likewise, we can neutralize an acid with a base (see Reaction 3 in Figure 3), but we end up with a soluble salt in our water.

With ion exchange resins, only the exchangeable ion is soluble. The counter ion, which is the resin bead itself, is not. This makes the separation after the exchange very easy. In the case of a softener, the resin has an exchangeable Na+. The hardness (Ca++ and Mg++) combined with the resin forms a very strong bond. The water, minus the hardness, passes on through because the resin is retained in the exchange column. Sodium (or potassium) replaces the hardness on an equivalent basis. This means that it will take two sodium ions from the exchange bead to replace a single calcium or magnesium ion.

In the case of demineralization, both the cations and the anions must be exchanged. This is done by using two different resins regenerated with acid and caustic respectively. The water passes through the cation exchanger first where the positive ions (cations) are exchanged for hydrogen ions (H+). (See Reaction 6 in Figure 3.) The acid solution is then passed through an anion exchanger where the acid is neutralized by the exchange of the acid ion (Cl-) for the hydroxyl (OH-) ion. (See Reaction 7 in Figure 3.)

Conclusion

The periodic table of the elements places all elements into families that help us predict properties and determine similarities. We have shown that there is a preferred coupling of certain elements to form reactions (such as $CaCO_3$ precipitation) that lead us to methods of removing those elements from water. This can be done either selectively (such as in softening) or completely (as in demineralization).•

References

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Michaud began his technical career with Rohm and Haas Company in 1964 and founded Systematix in 1982. He has been associated in direct sales for the past 23 years with The Purolite Company, a world-wide manufacturer of Ion exchange resins. He also serves on the Board of several diverse manufacturing companies.

Figure 3
Reactions

When a metal is dissolved in water, a basic, or alkaline solutions is created:

Reaction (1)

FeO	+	H_2O	→	$Fe(OH)_2$
iron oxide		water		iron hydroxide
Na_2O	+	H_2O	→	2 NaOH
sodium oxide		water		sodium hydroxid

Non-metals like sulfur and nitrogren also form oxides, but when dissolved into water, they form acids:

Reaction (2)

SO_3	+	H_2O	→	H_2SO_4
sulfur trioxide		water		sulfuric acid

Acids neutralize bases to form salt an water:

Reaction (3)

2NaOH	+	H_2SO4	→	Na_2SO_4		2HOH
caustic		acid		salt		water
$Ca(OH)_2$	+	$2HNO_3$	→	$Ca(NO_3)_2$	+	2HOH
lime		acid		salt		water

The formation of water is expressed as:

Reaction (4)

2H	+	O	→	H_2O
hydrogen		oxygen		water

Reaction (5)

$CaCl_2$	+	Na_2CO_3	→	2NaCl	+	$CaCO_3$
Calcium chloride		Sodium carbonate		Sodium chloride		Calcium carbonate (precipitate

Ion exchange with cation exchanger:

Reaction (6)

NaCl	+	$+H^+$	$+Na^+$	+	HCl
salt		cation exchanger	exhausted exchanger		acid

Ion exchange with anion exchanger:

Reaction (7)

HCl	+	OH^-	→	Cl^-	+	HOH
acid		anion exchanger		exhausted exchanger		water