Chemistry Primer for pH Measurements

This technical note is a general chemistry primer. First, the structure of the atom and the Bohr model are described. The period table and molecular bonds are then reviewed, followed by the definition of ions and ionic dissociation. Finally, the "mole", a quantity used to describe molecular concentrations is presented. These basic concepts are presented in the context of pH measurements.

Atomic Structure

In ancient Greek philosophy, "atomos", meaning "not divisible", was the smallest amount of matter (or particle) that could be conceived. This fundamental particle was thought to be indestructible. With the advent of experimental science in the sixteenth and seventeenth centuries, progress in atomic theory accelerated. Chemists soon recognised that liquids, gases and solids could be dissociated into their primary components, called "elements". These elements, through various types of chemical bonds, formed the building blocks of molecules.

Atoms are the fundamental form of elements. Atoms can combine in many different ways to form a multitude of different compounds, whose properties vary widely based on their atomic composition. Atoms of one hundred and twelve different elements have been identified to date.

The Rutherford Model In 1911, Ernest Rutherford formulated a theory of atomic structure that was the first visualization of the atom as a dense nucleus surrounded by orbiting electrons, which was called the "Planetary Model". Rutherford established that the mass of the atom is concentrated in its nucleus, which has a positive electric charge, while the electrons each have a negative charge. The atom is neutral because the total electronic and nuclear charges are equal. Rutherford only identified the positively charged component of the nucleus, called the proton. The Rutherford model of an atom was refined in 1913 by Niels Bohr, who postulated that electrons are arranged in definite shells (orbits), or quantum levels, at a defined distance from the nucleus.

Today, it is well-known that the nucleus comprises both neutrons and protons. The neutron, however, was not discovered until 1932, when James Chadwick realized that the nucleus has another particle having the same mass as the proton, but without an electric charge. In any given atom, the number of protons is equal to the number of electrons and defines the atomic number of the atom. The atomic number of an element determines its position in the "Periodic Table".

The Bohr Model The nuclear atom proposed by Rutherford was unstable. According to classical theories, this atom should collapse. It also failed to explain the discrete spectral lines of elements. To resolve these issues, Niels Bohr developed a hypothesis known as "The Bohr Theory of the Atom". Bohr's two fundamental assumptions were that:

1 There exist steady orbitals for electrons, so that when electrons orbit a nucleus at any of these special orbital radii, they do not radiate energy.

2 Electrons gain and lose energy as they move from one permitted radius (energy level) to another. They accept energy during excitation and release radiant energy during de-excitation. This energy is "quantized" according to Planck's relationship $E = hf = hc/\lambda$.

Bohr's model successfully explained the stability of the atom through his concept of "quantization". His "electron configuration" successfully predicted the spectral lines of hydrogen (figure 1), which had previously been studied by Kirchoff, Rydberg, Balmer, and others. The wavelength of light emitted when an electron moved from a higher energy level to a lower energy level was calculated with the formula

$$\lambda = hc / \Delta E$$

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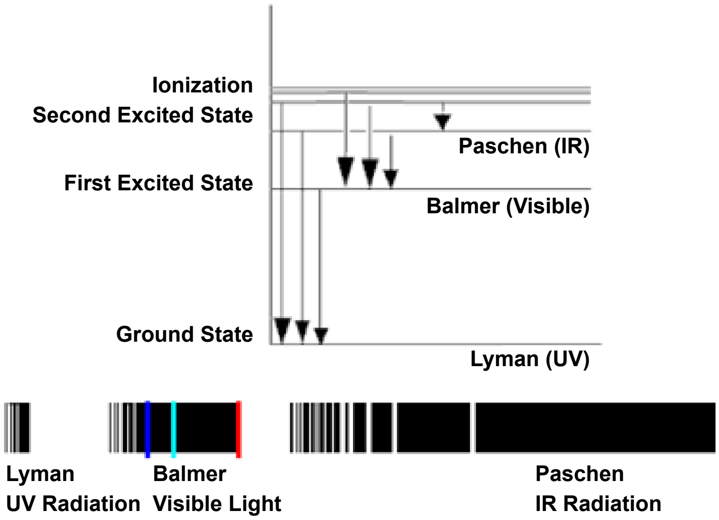


Figure 1
Discrete emission lines from hydrogen atom first predicted by Bohr's atomic model.

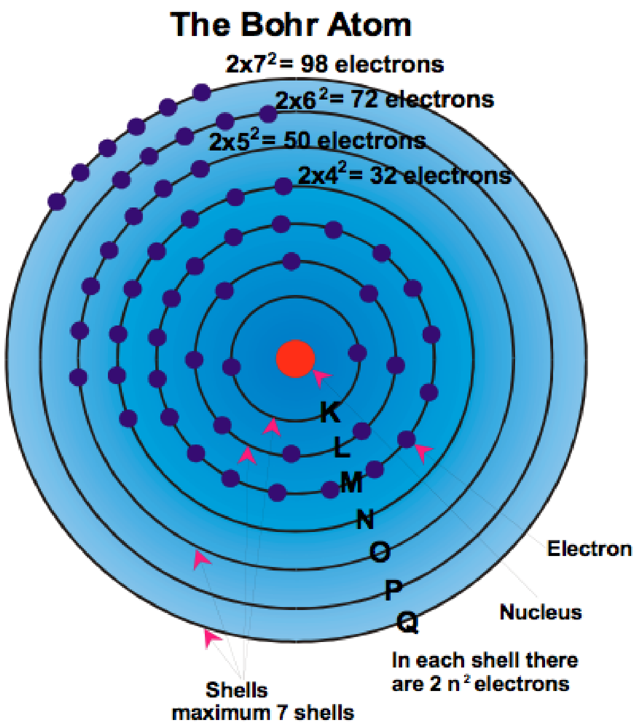


Figure 2:
Arrangement of electrons in shells

where ΔE represents the difference in the two energy level transitions. Bohr also provided a formula by which to compute the energy levels (in electron volts, eV):

$$E_n = -13.6\ Z^2 / n^2$$

where Z is the atomic number and n is the energy level. The ground state is n = 1, the first excited state is n = 2, the second excited state is n = 3, etc. 1 eV equals 1.6 x 10^{-19} Joules.

While Bohr's model is not completely correct, i.e., it fails to explain why the protons stay together in the nucleus, it had many features that were approximately correct. The correct theory of the atom is called quantum mechanics; the Bohr Model is an approximation to quantum mechanics that has the virtue of being much simpler.

Electron Shells In a multi-electron atom, each electron has its own orbital according to the Pauli principle (a law of quantum mechanics), so that many different kinds of orbitals can be occupied. A group of orbitals with the same, or nearly the same energy, is called a shell. The pattern of filled and unfilled shells is different for each element. This shell pattern gives the elements their distinctive characteristics and chemical reactivity.

The number of electrons equals the atomic number of the atom: for example, hydrogen has a single orbital electron, oxygen has 8, and uranium has 92.

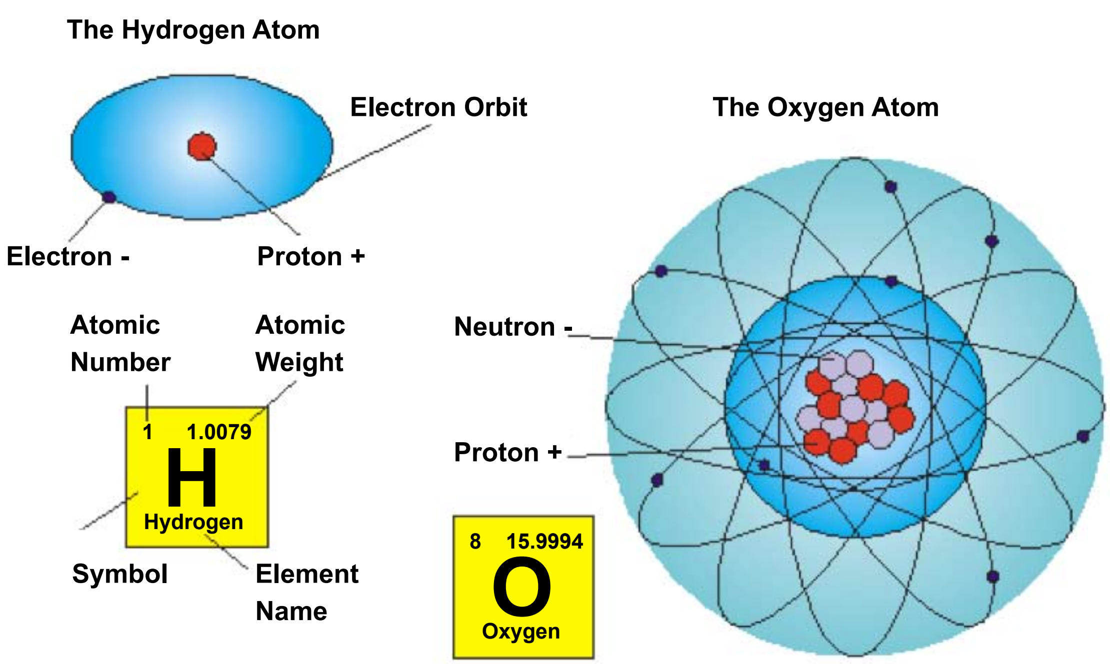
The electron shells are built up in a regular fashion from a first shell to a maximum of seven shells, each of which has an upper limit of the number of electrons that it can accommodate (figure 2). The shells are named from inner shell to outer shell: K-shell, L-shell … to Q-shell. The K-shell is complete with two electrons, the L-shell can hold up to eight electrons, the M-shell 18 electrons. In general, the nth shell can hold up to $2n^2$ electrons. The electrons in the outer shell determine the chemical behaviour of the atom. Atomic shells do not necessarily fill up with electrons in consecutive order. The electrons of the first 18 elements in the periodic table are added in a regular manner, with each shell being filled to a designated limit before a new shell is started.

Starting with the 19th element, however, the outermost electron starts a new shell before the previous shell is completely filled. A pattern can still be discerned, however, as electrons fill successive shells in a repetitive, back-and-forth pattern. The result is the regular repetition of chemical properties for atoms of increasing atomic weight that corresponds to the arrangement of the elements in the periodic table.

The Periodic Table In 1869, Dmitri Mendeleyev arranged all elements known at the time into a table according to their atomic mass. By doing so, he discovered that certain properties of the elements repeated themselves in a periodic way. Therefore, Mendeleyev grouped elements with similar chemical activities into vertical columns. This arrangement of the element became known as the Periodic Table. In the Periodic Table, the name, symbol, atomic number, and atomic weight are presented for each element, as illustrated for hydrogen and oxygen in figure 3.

Since Mendeleyev's time, additional elements have been discovered, so that the periodic table has been rearranged a few times. The table, as we know it today, is illustrated in figure 4. The elements are arranged horizontally from left to right by ascending atomic number (i.e., number of protons in the nucleus or orbiting electrons) in seven rows. Each row represents one of the seven electronic shells of the atom. Hydrogen, in position 1 of row 1, is the lightest element. The last element in the table is, for the time being, the artificial element "ununbium", taking the 112th position with an atomic mass of 277. The Periodic Table thus provides for a total of 118 elements. The 18 vertical columns group the elements according to their chemical activities (i.e. the numbers of electrons in their outer shell).

Figure 3 Representation of elements in the periodic table and example for hydrogen and oxygen elements.



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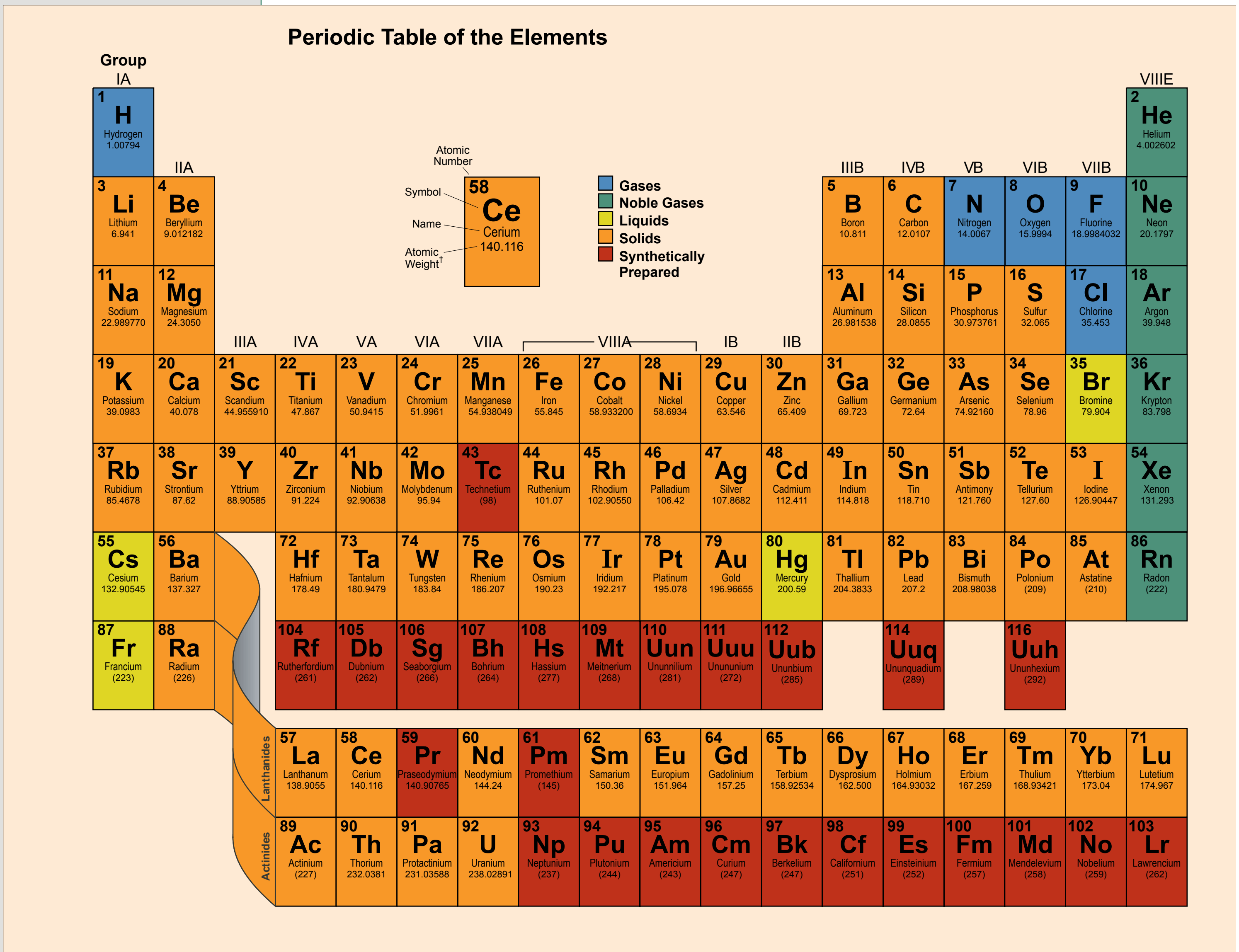

Figure 4 Periodic Table of the Elements

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The Molecule – Covalent Bonds

The molecule is the smallest unit of a chemical compound having the unique chemical properties of that compound. A molecule is comprised of atoms that are joined by an electrical force called a chemical bond. In the 1770s, Joseph Priestly and Antoine Lavoisier proved that water was not a basic element, as the ancient philosophers thought, but a compound of one atom of oxygen and two atoms of hydrogen – as expressed by the present-day formula H_2O.

Figure 5 Electron Configuration of Noble Gases

Electron Configuration of Noble Gases

	K	L	M	N	O	P	Q
Helium	2						
Neon	2	8					
Argon	2	8	8				
Krypton	2	8	18	8			
Xenon	2	8	18	18	8		
Radon	2	8	18	32	18	8	

In molecules, atoms are held together by sharing electrons (covalent bonds). In order to maximize these bonds, the atoms adopt specific positions relative to each other, i.e. each molecule has its own definite geometric structure. For instance in the water molecule, the two hydrogen atoms are bonded to the oxygen atom at an angle of 104.5°. As a consequence, there is a slight charge separation of the electronic clouds of the atoms so that water molecules have a dipole moment: specifically, the hydrogen atom electrons are attracted slightly towards the nucleus of the larger oxygen atom. In contrast, the CO_2 molecule is has a linear geometry (the O=C=O atoms form a straight line), and has therefore no dipole moment.

Not all elements can form molecules, however. If the outer shell of an atom is completely full, then the atom cannot normally form a bond (figure 5). Noble gases have atoms that contain either 2 electrons (He) or 8 electrons (Ne and Ar) in their outer shell. These lighter noble gases are non-reactive and cannot form molecules. However, this is not the case for the heavier noble gases. Since 1962, scientists have succeeded in producing compounds involving Kr, Xe and Rn. Any other element having an incomplete outer shell will more or less readily form a bond with other “non-noble” elements.

The number of bonds that an atom can form is called its valence. Oxygen has a valence of 2 as it needs another 2 electrons in order to fill its outer shell. Hydrogen has a valence of 1 because it has only one electron in its outer shell; it requires another electron to fill its shell, or it can give an electron to an atom which is one electron short. Two hydrogen atoms fulfil the needs of the oxygen atom and thereby form a molecule of water.

Salts – Ionic Bonds

The word “ion” derives from a Greek word meaning “traveller”. An ion is formed when a neutral atom gains or loses one or more electrons. An atom that loses an electron forms a positively charged ion called a cation, whereas an atom that gains an electron forms a negatively charged ion, called an anion.

When the elements sodium (Na) and chlorine (Cl) combine to form the molecule sodium chloride (NaCl), better known as table salt, they form an ionic bond (figure 6). The neutral sodium atom, having a single electron in its outer shell, will share this electron with the chlorine atom, which has 7 electrons in its outer shell. Again, the outer shell of each atom become, by this electron transfer, filled with 8 electrons.

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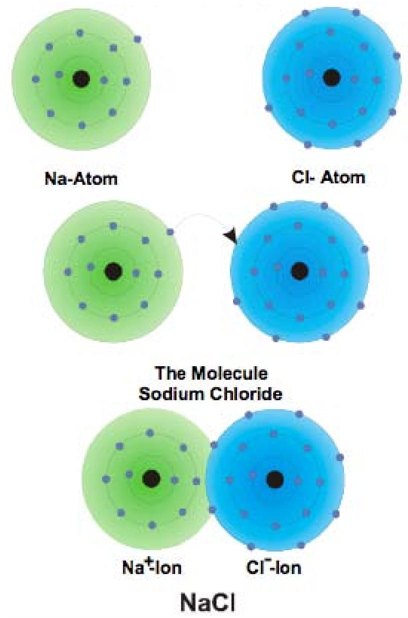


Figure 6 Ionic Bond of Sodium and Chlorine

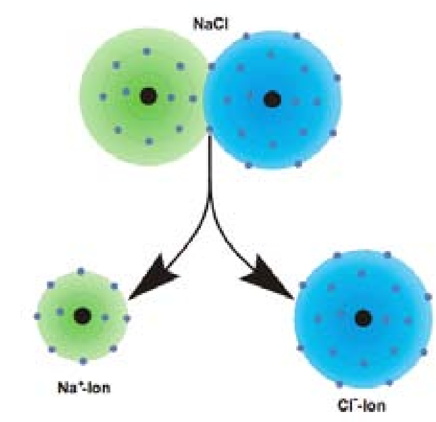


Figure 7 Dissociation of Sodium Chloride

In sodium chloride, the sodium atom becomes positively charged (by the loss of one electron to form a sodium ion Na^+), while the chlorine atom becomes a negatively charged (by the gain of one electron to form a chlorine ion (Cl^-). The new shell-structure of the sodium ion resembles that of a neon atom, and the new shell-structure of the chlorine ion resembles that of an argon atom. The two ions are held together by their electrostatic attraction.

If the ionic bond of a NaCl molecule is broken either through high temperature or through dissolution in water (see figure 7), the chlorine atom will keep its gained electron, and stays a negatively charged ion. The sodium atom will stay a positively charged ion. Under the influence of an electric field, ions will migrate (travel) to their opposite pole, and thereby create electrical conductivity in gases and liquids.

Water: The Universal Solvent

Water, by its polar nature, is an excellent solvent for three major groups of chemical compounds: salts, acids and bases. When dissolved in water, these chemicals separate into their underlying ions, namely, they dissociate. For example, when sodium chloride (NaCl) is placed into water, the polar forces of the water molecules will reduce the electrostatic attraction between the sodium and chlorine ions and cause them to dissociate (figure 7). The ions become surrounded by water molecules (hydrated) and can no longer recombine. Hydrochloric acid (HCl) will dissociate into H^+ and Cl^- ions and sodium hydroxide (NaOH) will dissociate into Na^+ and OH^- ions. The dissociation of salts, acids and bases in water causes the water to become an excellent conductor. The resulting solutions are called electrolytes (figure 8).

If two electrodes are immersed into an electrolytic solution, and a potential difference is applied to these electrodes, the anions will be attracted by the positively charged electrode (anode). When the anions reach the anode, they lose their charge (i.e., they loose their electrons). Similarly the positively cations will move towards the negatively charged electrode (cathode) and lose their charge by gaining electrons. The result is that a current can be measured in the electric circuit (figure 9).

Figure 8 Formation of an electrolyte solution.

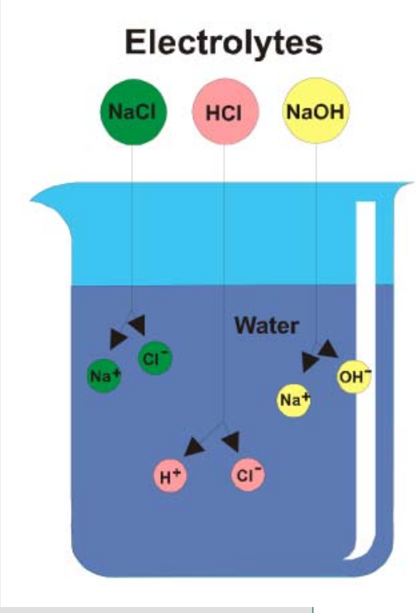
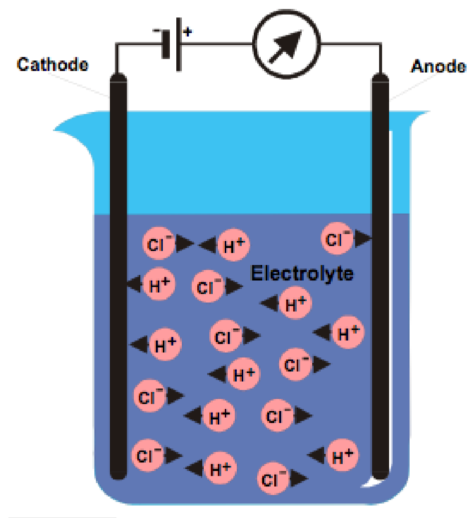


Figure 9 Measurement of current in electrolytic solution.



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Acids – Bases – Salts

In chemistry, there are three basic types of electrolytes: acids, bases, and dissolved salts.

Litmus is the oldest and most commonly used indicator of whether a solution is an acid or a base. It is a pink dye derived from lichen (a symbiotic association of a fungus and algae) and absorbed into paper. Litmus paper cannot be used to identify salts.

Acids are chemical compounds that, when dissolved in water, produce a concentration of hydrogen ions, (H^+ or protons) exceeding that of pure water. An acid is therefore a proton donor. Acids taste sour and turn Litmus paper red. Common acids include:

- Hydrochloric acid HCl
  Component of gastric juices
- Nitric acid HNO_3
  Dyes and explosives
- Acetic acid CH_3COOH
  Vinegar
- Formic acid $HCOOH$
  Dyeing and tanning
- Sulphuric acid H_2SO_4
  Batteries
- Phosphoric acid H_3PO_4
  Dental cement, fertilizer

Bases are chemical compounds that, when dissolved in water, produce an concentration of hydroxyl ions (OH^-) exceeding that of pure water. A base is therefore a proton acceptor. Bases feel slimy, taste bitter and turn Litmus paper blue. The most common bases are:

- Sodium hydroxide $NaOH$
  Drain and oven cleaner
- Calcium hydroxide $Ca(OH)_2$
  Slated lime (mortar for construction)
- Aluminium hydroxide $Al(OH)_3$
  Raw material for aluminium compounds
- Potassium hydroxide KOH
  Soft soap
- Magnesium hydroxide $Mg(OH)_2$
  Milk of magnesia
- Ammonia NH_3
  Household cleaners

When an acid and a base are combined, a neutralization reaction occurs. This reaction takes place very rapidly and generally produces water and a salt. For example, sulphuric acid (H_2SO_4) and sodium hydroxide ($NaOH$), yield water and sodium sulphate (Na_2SO_4): $H_2SO_4 + 2NaOH = 2H_2O + Na_2SO_4$.

Salts are produced from acids or bases by substituting the H^+ ion with a base part or by substituting the OH^- ion with an acid part. The resulting cations and anions combine to form an electrically neutral compound called a salt. For example:

- Sodium nitrate
  $NaNO_3 = Na^+ + NO_3^-$
- Aluminium sulphate
  $Al_2(SO_4) = 2Al^{3+} + 3SO_4^{2-}$
- Calcium phosphate
  $Ca_3(PO_4)_2 = 3Ca^{2+} + 2PO_4^{3-}$

The Mole: Measuring Quantities of Molecules

"The mole is the SI unit of an amount of substance equal to the quantity containing as many elementary units as there are atoms in 0.012 kg (12g) of carbon-12. The elementary entities must be specified and may be atoms, molecules, ions, electrons or other particles. The unit was established in 1971 for international use."

(The Oxford Dictionary)

The number of elementary particles contained in 12g of carbon-12 (the standard reference atom) is 6.0221367×10^{23}. This number is known as the Avogadro's number in honour of the Italian physicist Amedeo Avogadro, who postulated in 1811 that equal volumes of gases, at equal temperatures and pressures, contain the same number of molecules.

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A mole, therefore, is an amount of any substance that weighs, in grams, as much as the numerically equivalent atomic weight of that substance.

1 mole H_2	= 2 g
1 mole H_2O	= 18 g
1 mole Cl_2	= 71 g
1 mole Rn	= 222 g
1 mole HCl	= 36.5 g
1 mole NaOH	= 40 g

Hydrogen Ion Concentration in Aqueous Solutions

Not only does water dissolve and dissociate electrolytes, but water itself disassociates. Specifically, water molecules can dissociate into hydrogen ions (H^+) and hydroxyl ions (OH^-) through the reaction: $H_2O \Leftrightarrow H^+ + OH^-$. These hydrogen ions have the following charateristics:

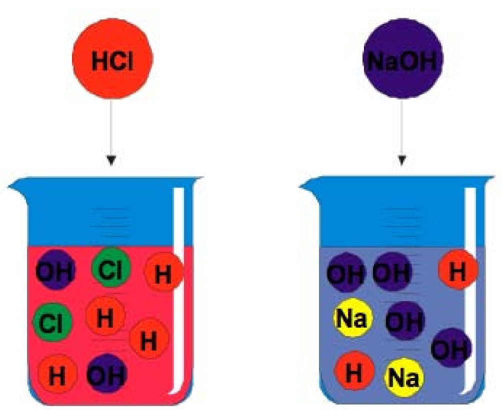
H^+ = Positive charge and associated with acidity

OH^- = Negative charge and associated alkalinity

If the amount of hydrogen ions equals the amount of hydroxyl ions, then the water is neutral. In clean, neutral water only one out of 10 000 000 (10^7) water molecules will dissociate.

In reality, hydrogen ions do not exist freely in solution but are associated with water molecules. The ionization of water should thus be written more correctly as: $2HOH \Leftrightarrow H_3O^+ + OH^-$. H_3O^+ is called the hydronium ion and is, in aqueous solutions, the ion responsible for acidic properties. For simplicity, equations are normally written using H^+.

By dissolving an acid in neutral water, the H^+ concentration is increased by the H^+ ions, which are produced by the dissociation of that acid (figure 10). As a result, the water changes its properties, i.e. it tastes sour like vinegar or lemon juice, and becomes corrosive and dissolves metals.



Acid solution

Alkaline solution

Figure 10 Formation of an acid and base aqueous solution.

By dissolving a base in neutral water, the OH^- concentration is increased by the OH^- ions which are produced by the dissociation of that base (figure 10). There, the relative amount of the H^+ ions will be reduced. The water will again change its properties, i.e. it tastes bitter and feels slimy like wet soap.

In both cases, the water becomes an aqueous solution. All aqueous solutions of acid and bases owe their chemical activity to their relative hydrogen ion (H^+) and hydroxyl ion (OH^-) concentration.

The hydrogen ion concentration in an aqueous solution is expressed by the amount of non-dissociated water molecules in relation to one hydrogen ion, i.e.

- if one H^+ is found in 100 water molecules we write 1:100 or $1/10^2$ or 10^{-2}
- if one H^+ is found in 10,000,000 water molecules we write 1:10,000,000 or $1/10^7$ or 10^{-7}, and
- if one H^+ ion is found in 1,000,000,000 water molecules we write 1:1,000,000,000 or $1/10^9$ or 10^{-9}.

The ion product of dissociated H^+ ions and dissociated OH^- ions in water has been found to be a constant of 10^{-14} (mole/liter) at 22°C. Thus, when the concentration of H^+ ions and OH^- ions in pure water are equal, the H^+ ion concentration must be 10^{-7} and, of course, the OH^- ion concentration must be 10^{-7} as well.

This automatically leads to the definition of pH value, which is expressed as the negative base 10 logarithm of the active hydrogen ion concentration in an aqueous solution, or in mathematical terms:

$$pH = -\log[H^+].$$

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