Practical Analytical Instrumentation in Online Applications

- An Overview:

- Basic Chemistry
- Electrochemical Cells
- pH & Conductivity Measurement

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Practical Analytical Instrumentation in On-Line Applications

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1

Basic Chemistry

Objectives

When you have completed this chapter you should be able to:

- Define the differences between elements, compounds and mixtures
- Explain the difference between organic and inorganic chemistry
- Describe the structure of an atom
- Show how the periodic table is formed and describe the different properties of elements
- Show how ions are formed and understand both covalent and ionic bonding
- Understand chemical formulae and the use of chemical equations
- Explain atomic weight and molar concentrations
- Discuss the difference between acids and bases and explain oxidation-reduction

1.1 Introduction

1.1.1 Elements, compounds and mixtures

All substances may be divided into three classifications: elements, compounds and mixtures.

The simplest forms of matter are ***elements*** — substances that cannot be split into simpler substances by a chemical reaction. As shown in Figure 1.1, there are over 100 known elements classified in the periodic table and these form the building blocks of all chemicals.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Unq	Unp	Unh												

Figure 1.1
The periodic table

A ***compound*** is formed by two or more elements which are always combined in the same fixed ratio. Thus, for example, water is a compound of hydrogen and oxygen, shown by its chemical formula H_2O, which is always formed from two parts hydrogen and one part oxygen (Figure 1.2). Compounds are often difficult to split into their elements and can only be separated by chemical reactions.

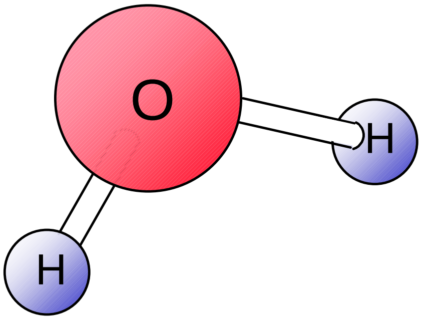


Figure 1.2
Water (H_2O) — a compound formed from two parts hydrogen and one part oxygen.

The smallest particle of an element or compound that normally exists by itself and still retains its properties is called a molecule. Normally a molecule consists of two or more atoms — sometimes even thousands. However, as we shall see later, a molecule can also exist as a single atom called a ***monatomic molecule.***

Elements and compounds are pure substances whose composition is always the same. In reality, pure substances are rarely encountered and most are ***mixtures*** of compounds or elements that are not chemically combined and in which the proportions of each element or compound are not fixed (Figure 1.3).

Since the elements or compounds making up the mixture each keep their own properties they can usually be separated fairly easily by physical means.

When a mixture has the same properties and composition throughout, (e.g. a mixture of sugar and water in which the sugar is thoroughly dissolved in the water) it is called a ***homogeneous*** mixture or a ***solution***.

When the composition and properties of a mixture vary from one part to the other it is called ***heterogeneous***. This might take the form of a suspension in which fine particles of a solid are suspended in a liquid and are not dissolved. Another type of heterogeneous mixture is a two-phase mixture: e.g. a mixture of oil and water in which the oil floats on the water as a separate layer.

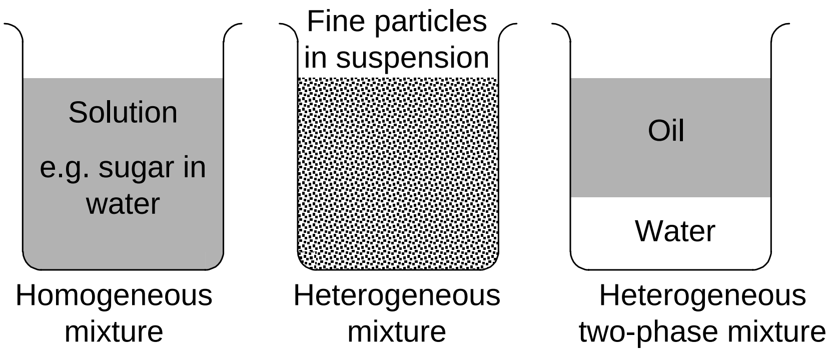


Figure 1.3
Various types of mixtures

1.1.2 Organic and inorganic chemistry

In the study of elements and their components, a distinction is made between what is termed organic and inorganic chemistry.

Originally organic chemistry concentrated on the study of substances found in living organisms. Now, however, it extends to cover all (with a few exceptions) of the compounds of carbon. The vast number of organic compounds (well over two million) include plastics, fibres, drugs, cosmetics, insecticides, foods, etc., and are made possible by the ability of the carbon atom to bond to itself and form a virtually unlimited chain or ring.

Inorganic chemistry is the study of that which is left over — those substances that do not form bonds with carbon.

1.2 Atomic structure

At one time the atom was considered to be the ‘fundamental particle’ — the smallest bit of matter that could be conceived. And indeed, since all atoms of any given element behave in the same way chemically, the atom is the smallest entity to be considered from a chemical viewpoint.

In considering the basic construction of an atom it is usual to consider it as being composed of three elementary sub-atomic particles: protons, neutrons and electrons. It is the number of protons, neutrons and electrons that any atom contains that distinguishes one element from another.

The main mass of the atom comprises the nucleus, which consists of protons and neutrons. The proton has a positive charge and a relative mass of 1 whilst the neutron has a similar mass but no charge.

The nucleus is surrounded by a cloud of electrons each having a negative charge and a mass nearly 2000 times smaller than the proton. In its normal state, an atom has the same number of electrons as protons and is, therefore, electrically neutral.

The simplest structure is the hydrogen atom, which comprises a single proton and a single electron (Figure 1.4).

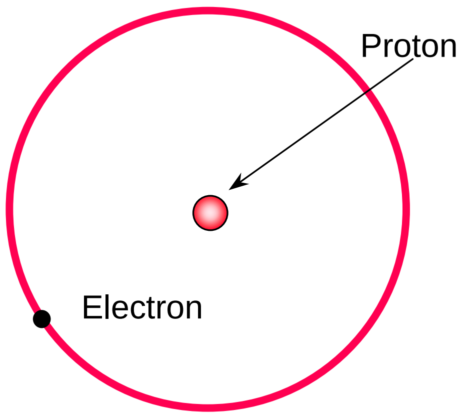


Figure 1.4
Basic structure of a hydrogen atom comprising a single proton and a single electron.

An element is determined by the number of protons in the nucleus — its ***atomic number.*** Since the atomic number defines the element, any atom with 6 protons is carbon, irrespective of the number of neutron or electrons (normally 6 of each).

However, because the number of neutrons in the nucleus may not always be the same as the number of protons, an atom is also defined in terms of the total number of protons and neutrons in the nucleus — called its ***mass number*** (not to be confused with its atomic mass). Carbon, for example would normally have 6 protons (atomic number = 6) and 6 neutrons giving a mass number of 12. However, carbon can also exist in other forms, called ***isotopes***, in which the nucleus contains 7 or even 8 neutrons — giving a mass number of 13 or 14 respectively.

The three carbon isotopes are distinguished from one another by writing the mass number after the name of symbol of the element. Thus, as shown in Figure 1.5, carbon with 6 neutrons is called Carbon-12; with 7 neutrons is called Carbon-13; and with 8 neutrons is called Carbon-14.

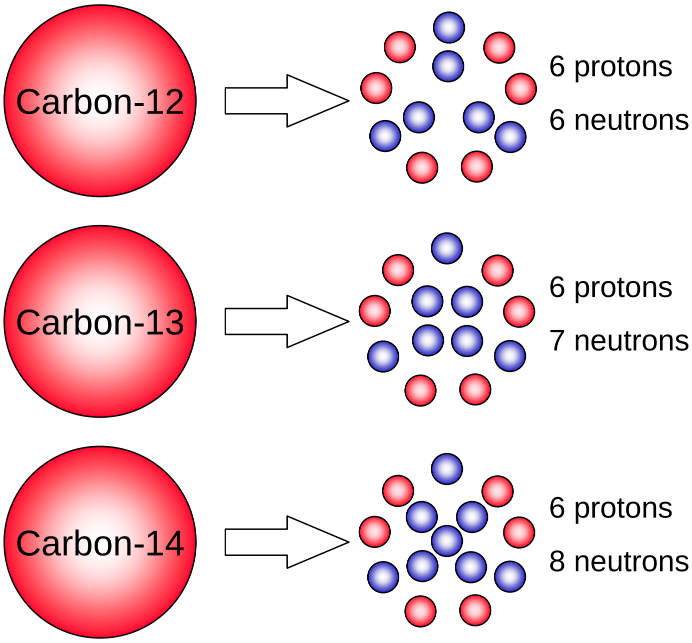


Figure 1.5
The three isotopes of carbon which are distinguished from one another by writing the mass number after the name of symbol of the element.

Electron shells

With the electrons forming a cloud around the nucleus, the position of any electron is defined in terms of the probability of finding it at some distance from the nucleus. Consequently, it is convenient to visualise the electrons moving around the nucleus of an atom in the same way as planets move around the sun.

This solar-system model visualises the electrons arranged in definite shells or energy levels. Each shell has an upper limit to the number of electrons that it can accommodate and each is built up in a regular fashion from the first shell to a total of seven shells. The first shell can accommodate 1 or 2 electrons; the second shell a maximum of 8; the third a maximum of 18; the fourth 32 and so on with successive shells holding still larger numbers.

In the study of chemistry, it is the electrons in the outermost shell — those which are added last to the atom's structure — that determine the chemical behavior of the atom. This outer shell is called the ***valance shell*** and the electrons in it are called ***valance electrons***. For the first two shells (the first 10 elements) matters are simple and each shell is filled before a fresh one is started. However, in later elements the outer shell develops before the previous one is completed.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Unq	Unp	Unh												

Figure 1.6
The full periodic table

Chemical symbols

As shown in Figure 1.1, each element has its own unique symbol that, in most cases, is formed from one or two letters of the element’s English name: e.g. H for hydrogen; He for helium; Li for lithium. Note that the first letter is always capitalised and, where there is a second letter, this is always written in lower case. The symbols of some elements are derived from their Latin names (Table 1.1): Na for sodium from its Latin name Natrium; Au for gold from its Latin name Aurum; Pb for lead from its Latin name Plumbum; etc. An exception to this derivation is tungsten whose symbol W is derived from its German name Wolfram.

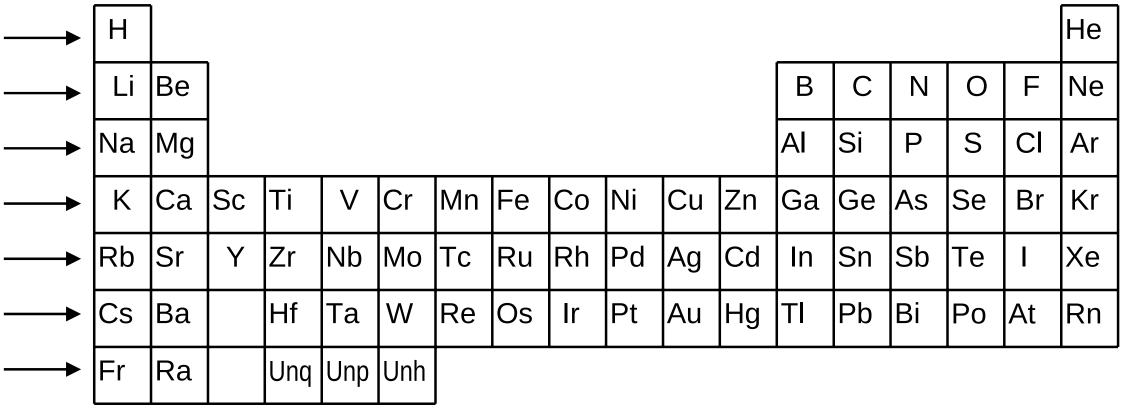
Table 1.2
Symbols of elements derived from their Latin names.

Element	Atomic Number	Latin Name	Symbol
Sodium	11	Natrium	Na
Potassium	19	Kalium	K
Iron	26	Ferrum	Fe
Copper	29	Cuprum	Cu
Silver	47	Argentum	Ag
Tin	50	Stannum	Sn
Antimony	51	Stibium	Sb
Gold	79	Aurum	Au
Mercury	80	Hydrargyrum	Hg
Lead	82	Plumbum	Pb

1.3 Periodic table

The periodic table (Figure 1.1) is an arrangement of the elements, in order of their increasing atomic numbers, in which a wide range of chemical and physical information is arranged in a systematic way.

As shown, there are seven rows, called ***periods***, with the atomic number increasing by one element from left to right.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Unq	Unp	Unh												

The vertical columns or groups are numbered using roman numerals and separate the elements into families having the same number of electrons in the outer shell and similar chemical properties.

As shown in Figure 1.7, about 75% of the elements are made up of what are called metals. Except for mercury, metals are solid and are characterised by high conductivity (both electrical and thermal); high malleability (the ability to be formed or hammered into different shapes); and high ductility (the ability to be drawn into a thin wire).

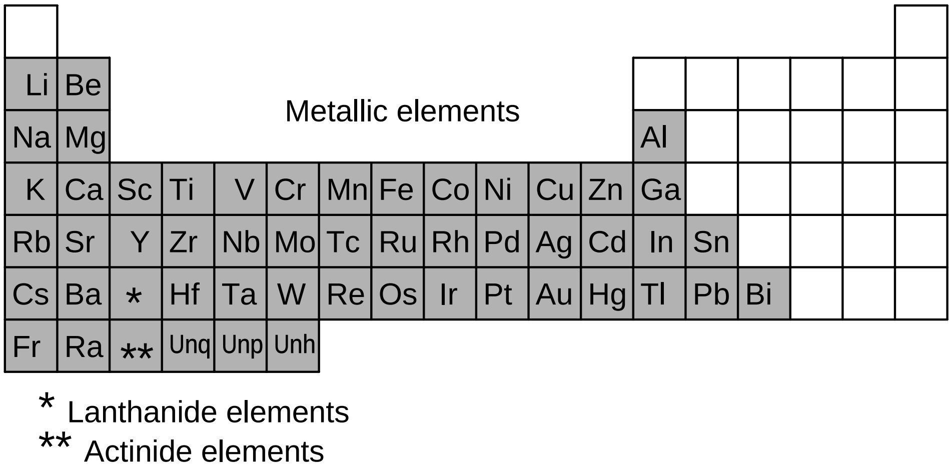

Metallic elements
Li Be
Na Mg Al
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn
Cs Ba * Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi
Fr Ra ** Unq Unp Unh
* Lanthanide elements
** Actinide elements

Figure 1.7
About 75% of the elements are made up of metals

Moving to the right, the elements gradually become less metallic and, on the extreme right (Figure 1.8), are termed non-metals. Non-metals can be solid (carbon being the most commonly observed) liquid (bromine) or gas (oxygen, nitrogen) and generally have poor conductivity, malleability and ductility.

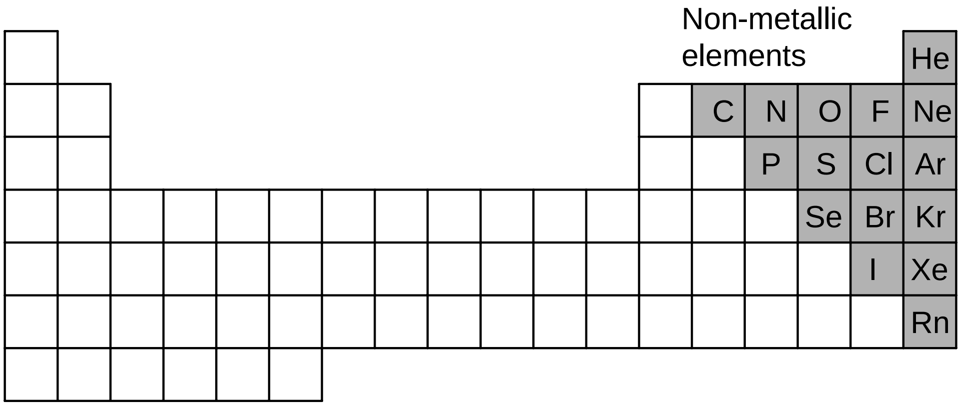

Non-metallic elements
He
C N O F Ne
P S Cl Ar
Se Br Kr
I Xe
Rn

Figure 1.8
Non-metal elements

Somewhere in between the metallic and non-metallic elements are the metalloids (Figure 1.9) that behave mainly like non-metals except that their electrical conductivity, although not good, is closer to metals. These elements are thus often termed semiconductors.

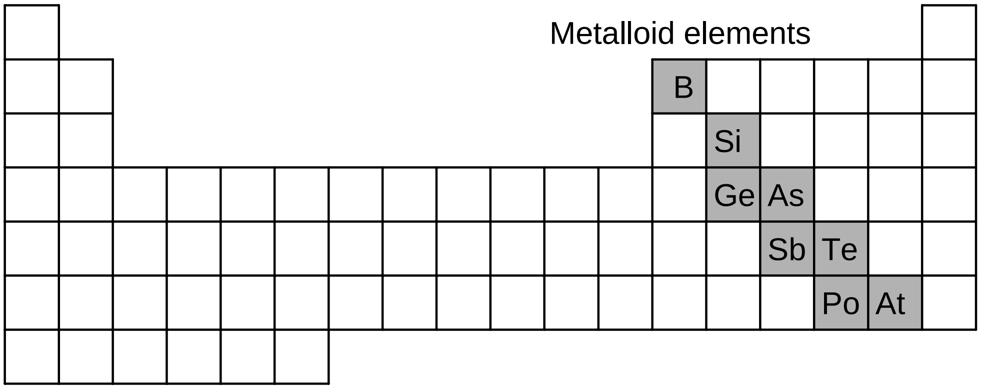

Metalloid elements
B
Si
Ge As
Sb Te
Po At

Figure 1.9
The metalloid or semiconductors elements

1.4 Properties of elements

Elements to the extreme left of the periodic table (Figure 1.10), in Group I are, with the exception of hydrogen*, called ***alkali metals*** — metals that react with water to form alkaline solutions. All have only one valence electron (one electron in their outer shell) which is easily lost in reactions. Indeed, moving down the group from lithium, sodium, potassium, rubidium, caesium, and francium, their reaction with water becomes increasingly more violent and all need to be stored under oil because of this reactivity.

*Hydrogen owes its location in Group I to its electron configuration rather than its chemical properties.

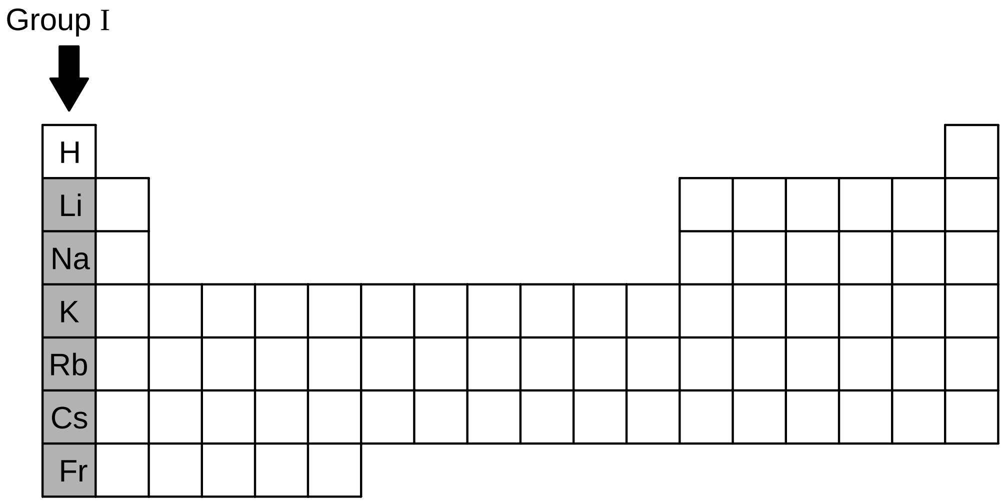


Figure 1.10
Group I — the alkali metals

The metals of Group II (Figure 1.11) have two fairly loosely bound valance electrons and, although they are also strongly reactive, are not as reactive as Group I elements. Group II elements tend to be found as naturally occurring mineral deposits in the ground or in the sea and are, therefore called the ***alkaline earth metals***.

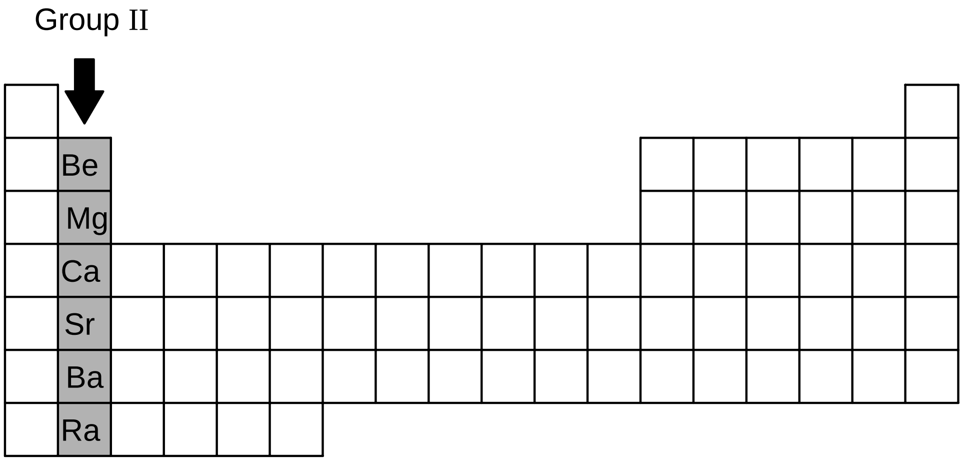


Figure 1.11
Group II — the alkali earth metals

At the far right hand side of the periodic table (Figure 1.12) are the Group VIII (also know as Group O) elements that form the noble or inert gases. The term noble indicates that the element is chemically inert or inactive.

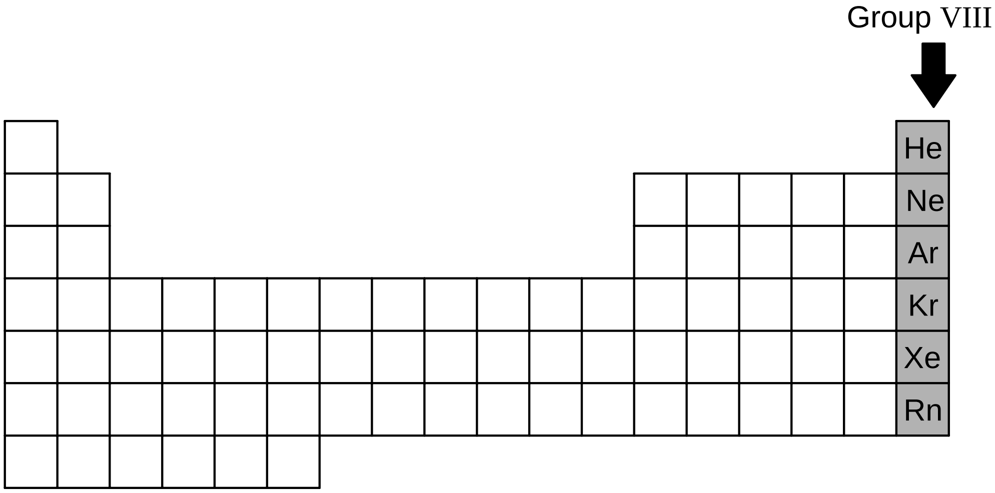


Figure 1.12
Group VIII — the noble or inert gases

Noble gases – helium, neon, argon, krypton, xenon and radon – all have a full outer shell which accounts for their extreme stability and unwillingness to form compounds. Indeed, at normal temperatures, the lighter noble gases form no compounds whatsoever and exist as monatomic (single-atom) molecules.

In contrast, gases such as hydrogen, nitrogen, oxygen, fluorine, and chlorine react with each other to form ***diatomic*** (two-atom) molecules (Figure 1.13) e.g. H_2, N_2, O_2, F_2, and Cl_2. The Non-metallic elements bromine and iodine also exist as diatomic molecules: Br_2 and I_2.

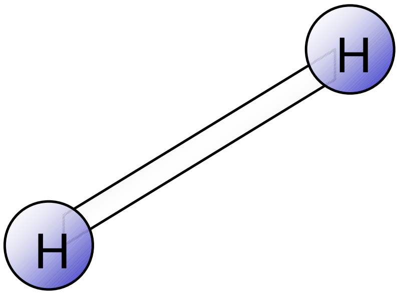


Figure 1.13
Hydrogen exists as a two-atom or diatomic molecule (H_2)

Another important group that needs to be considered is Group VII – the halogens (Figure 1.14). The elements in this group – fluorine, chlorine, bromine, iodine and astatine – are all non-metals and are characterised by having seven valence electrons.

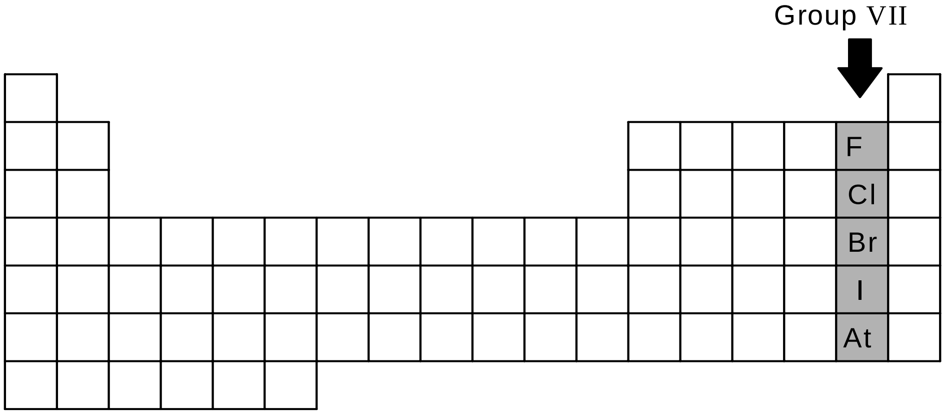


Figure 1.14
Group VII — the halogens

1.5 Formation of ions

Earlier we stated that the nature of the element is determined by its atomic number – the number of protons within the nucleus – and that it can gain or lose electrons. We also saw how the electrons in an atom are arranged in shells.

Because of the increasing distance of successive shells from the nucleus, the outer electrons are further away from the nucleus and are thus held less tightly. The result is that less energy is required to remove an electron from the 2nd shell than from the 1st shell and still less to remove an electron from the 3rd shell than the 2nd shell. Thus, referring to the periodic table, the energy required to remove an electron from the outer shell of an atom decreases from the top to the bottom (Figure 1.15).

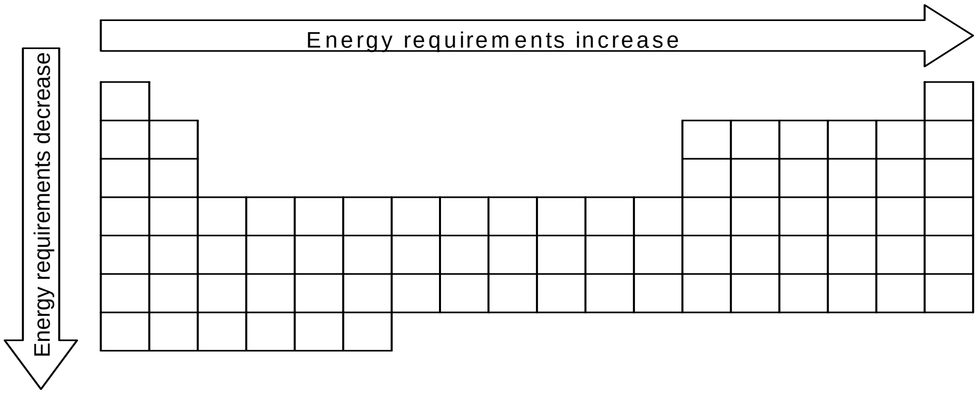


Figure 1.15
The energy required to remove an electron from the outer shell of an atom increases from left to right and decreases from the top to the bottom

In addition, elements to the left of the table have loosely held valence electrons that are easily lost. Now, moving from left to right, as electrons are added to the outer shell, an effectively increasing charge binds them more and more tightly to the nucleus.

It can thus be seen that it is very difficult for elements in the upper right-hand corner to lose electrons and indeed elements with nearly completed shells will tend to attract electrons.

Figure 1.16 shows a sodium atom (atomic number 11) in which the first and second shells are complete and there is one valence electron. Assume now that the atom loses the electron in its outmost shell. What will be the result?

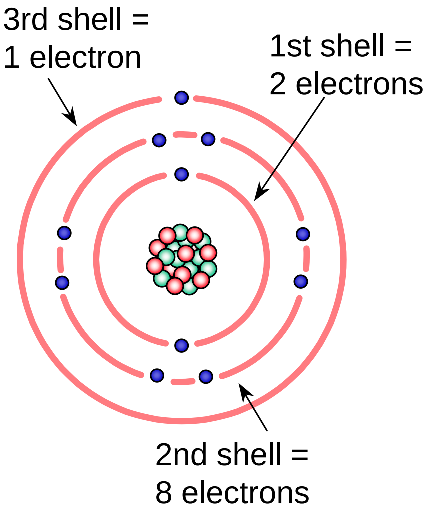

3rd shell =
1 electron
1st shell =
2 electrons
2nd shell =
8 electrons

Figure 1.16
Basic structure of a sodium atom

Firstly, since the nucleus has been unaffected and it still has 11 protons (as well as 11 neutrons) it will continue to remain sodium.

The main effect will be that the total charge of the atom will no longer be neutral but will be unbalanced by the absence of the negatively charged electron. The result is that the atom will now have a net positive charge. Since, by definition, an atom is neutral, the change in its charge by losing the electron has, in effect created a new particle called an ***ion***. A positively charged ion is called a ***cation*** (pronounced CAT-ion).

The loss of the electron (e^-) from the sodium atom creates an ion with a net charge of +1 and the particle's change in status from a sodium atom to a sodium cation (Figure 1.17) could thus be indicated by the symbol Na^{1+}. In practice the 1 is implied and the symbol is thus written Na^+.

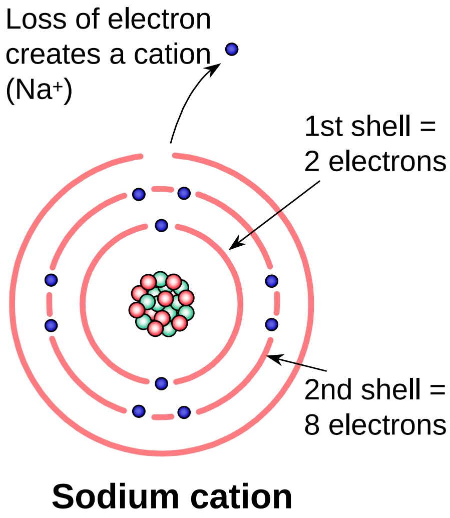

Loss of electron
creates a cation
(Na+)
1st shell =
2 electrons
2nd shell =
8 electrons
Sodium cation

Figure 1.17
Formation of sodium cation

If a magnesium atom (atomic number 12) with *two* valence electrons (Figure 1.16) should lose them, then the resulting cation will be unbalanced by the absence of *two* electrons and thus have a net positive charge of +2. In this case the particle's change in status from a magnesium atom to a magnesium cation (Figure 1.18) is indicated by the symbol Mg^{2+}.

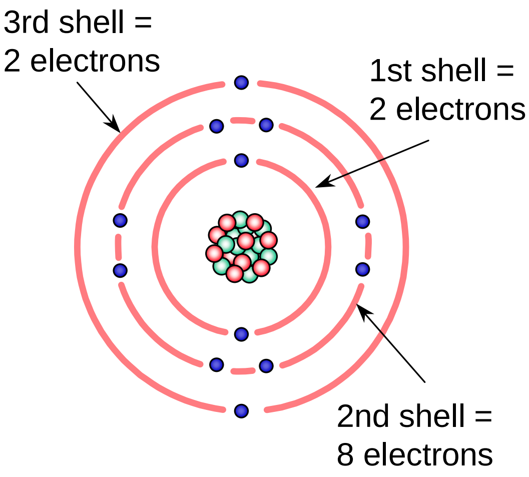

3rd shell =
2 electrons
1st shell =
2 electrons
2nd shell =
8 electrons

Figure 1.18
Basic structure of a magnesium atom

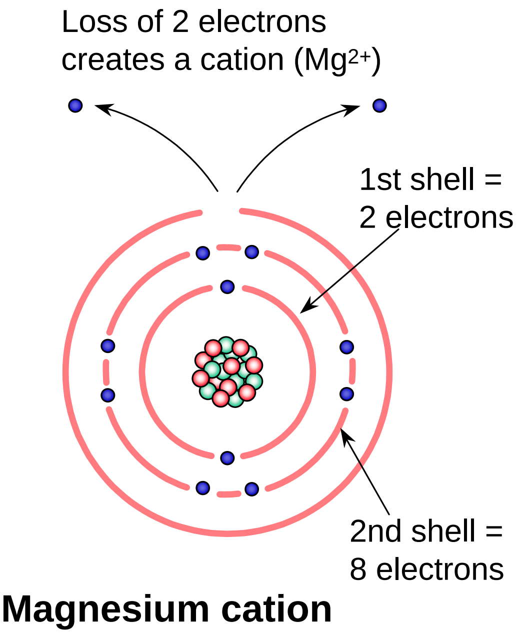

Loss of 2 electrons
creates a cation (Mg2+)
1st shell =
2 electrons
2nd shell =
8 electrons
Magnesium cation

Figure 1.19
Formation of magnesium cation

If we examine the structure of a chlorine atom (atomic number = 17), as depicted in Figure 1.20, it can be seen that the outer (third) shell contains only 7 electrons. And if it should capture an electron and make its outer shell complete (Figure 1.21) its overall charge will become negative. A negatively charged ion is called an anion (pronounced AN-ion).

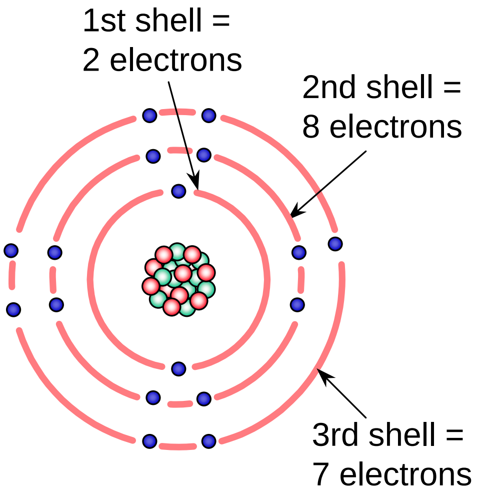

1st shell =
2 electrons
2nd shell =
8 electrons
3rd shell =
7 electrons

Figure 1.20
Basic structure of a chlorine atom

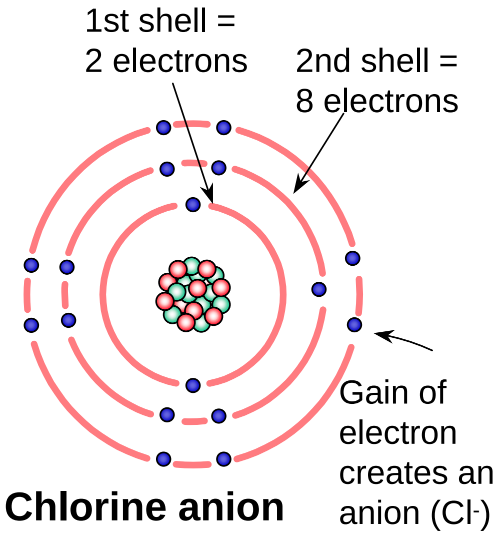

1st shell =
2 electrons
2nd shell =
8 electrons
Gain of
electron
creates an
anion (Cl-)
Chlorine anion

Figure 1.21
Formation of chlorine anion

The gain of the electron (e^-) into the outer shell of the chlorine atom, creates an ion with a net charge of -1 and the particle's new status as a chlorine anion is indicated by the symbol Cl^- -- again with the 1 being implied.

1.6 Bonding

Earlier, we described a compound as a combination of two or more elements. The elements that are combined to form compounds are held together by bonding forces called ***chemical bonds.*** The two major bonding forces are ***ionic bonding*** and ***covalent bonding.***

1.6.1 Ionic bonding

Ionic bonding is based on the fact that opposite charges attract!

We have already seen how Group I and II elements have loosely held valence electrons that are easily lost and how elements with nearly completed shells will tend to attract electrons.

Thus a sodium atom with a single valence electron will give it up easily to, for example, a chlorine atom with 7 valence electrons (Figure 1.22).

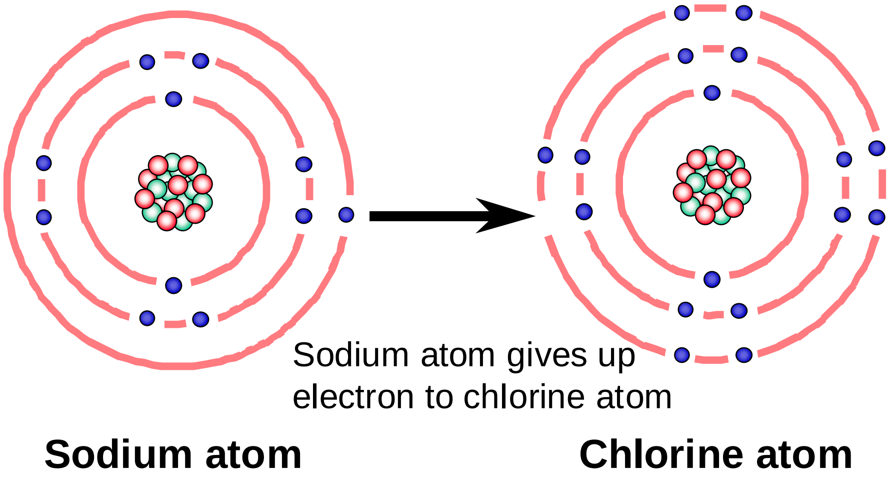


Figure 1.22
Sodium atom gives up an electron easily to a chlorine atom with 7 valence electrons

The sodium cation, with a net charge of +1 and a chlorine anion having a net charge of -1 are attracted to each other and thus form an ionic bond. This ionic bond, formed between a sodium cation (Na^+) and a chlorine anion (Cl^-), results in the compound sodium chloride (Na^+Cl^-) or common salt (Figure 1.23). In practice the ionic charges are omitted from the formula which then becomes NaCl.

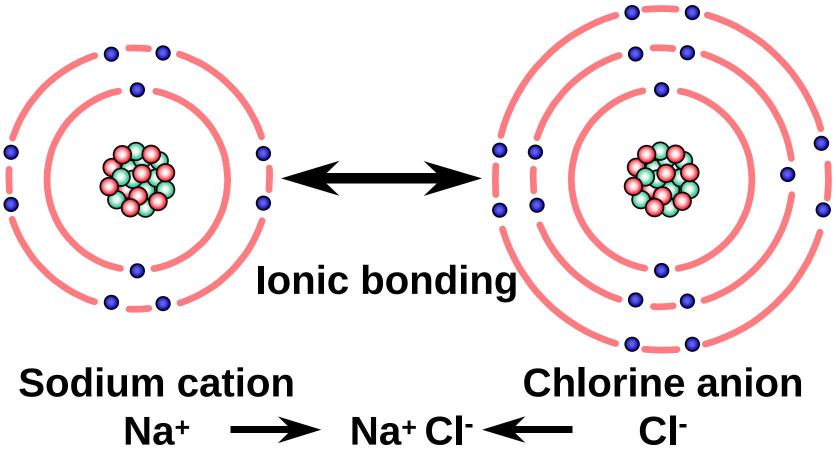


Figure 1.23
The ionic bond formed between a sodium cation (Na^+) and a chlorine anion (Cl^-) results in the compound sodium chloride (Na^+Cl^-)

Another example of an ionic compound formed in this manner is that of magnesium and oxygen. Here, a magnesium cation (Mg^{2+}) having a net charge of +2, combines with an oxygen anion (O^{2-}) having a net charge of -2. The ionic bonding results in the compound magnesium oxide ($Mg^{2+}O^{2-}$) — normally written as MgO.

Ionic compounds thus exist as a collection of electrically charged positive and negative ions –

with each positive ion surrounding itself with as many negative ions as it can, and each negative ion surrounding itself with as many positive ions as it can.

The resulting structure consists of a regular pattern of alternate positive and negative ions, in which no individual molecules can be identified. This regular arrangement of positive and negative ions continues indefinitely in three dimensions throughout the whole structure and is stacked together to form a crystal lattice (Figure 1.24).

Such ionic crystals are hard and brittle with high melting points. Because, at room temperature, the ions are bound and are not free to move, ionic compounds do not normally conduct electricity. However, when melted or dissolved in water, the ions are freed and the materials become conductive.

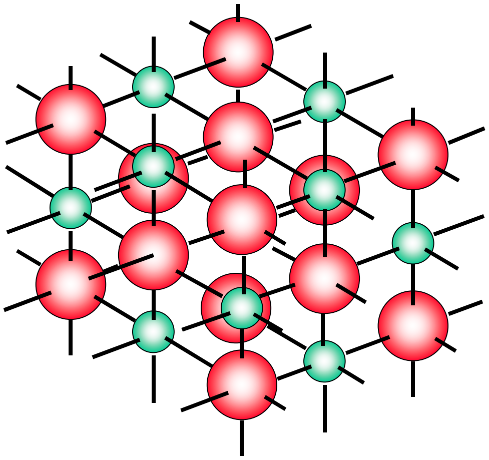


Figure 1.24

Ionic compounds exist as collections of ions stacked together to form a crystal lattice

The ionic compounds formed in this fashion between metals and non-metals are called ***salts***.

1.6.2 Covalent bonding

Covalent bonding is a more complex arrangement than ionic bonding. Here, the valence electrons are actually shared between the atoms so that each acquires a stable outer shell.

When two atoms of hydrogen are brought together their electrons begin to feel the attraction of both nuclei (Figure 1.25). As the distance continues to decease, there is an increasing probability of finding either electron near either nucleus and at some point, each hydrogen atom shares an electron and the two are thus bonded together to form an H_2 molecule. A less accurate, but more easily visualised, analogy is that the electrons form a figure-of-eight path (Figure 1.26) around the two nuclei to form the H_2 molecule.

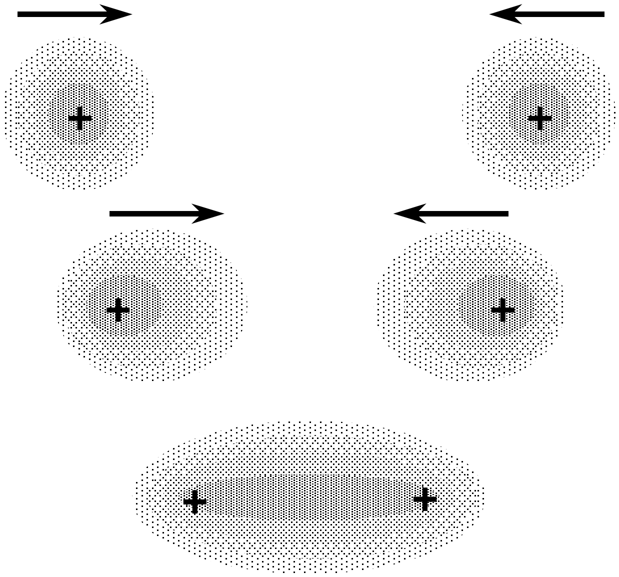


Figure 1.25
When two hydrogen atoms are brought together, at some point a bond is formed and each hydrogen atom shares an electron with the other to form an H_2 molecule

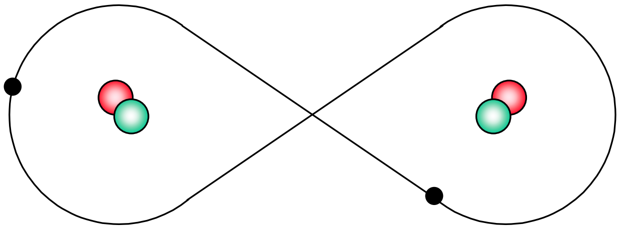


Figure 1.26
The electrons can be visualised as forming a figure-of-eight path around the two nuclei to form an H_2 molecule

In ionic bonding the ions exist separately. In covalent bonding, however the net molecular charge is neutral. In the case of hydrogen, the covalent bond is formed by a single pair of electrons – with the pair usually connected by a single dash (–):

H – H

Another example of a single-pair covalent bond is chlorine (Figure 1.27). When chlorine atoms approach each other (each with an electron valence of seven) covalent bonding occurs when a pair of electrons are shared (one from each atom) so that each atom now has a stable outer shell of 8 electrons. Again the molecule formed by this single-pair bond is represented by: Cl – Cl

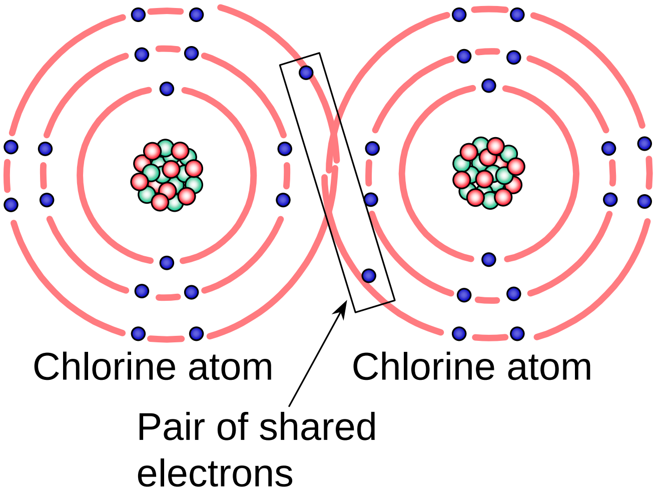


Figure 1.27
Covalent bonding of chlorine atoms occurs when a pair of electrons is shared so that each atom now has a stable outer shell of 8 electrons

Yet another single-pair covalent bond can be formed by, for example, hydrogen and chlorine (Figure 1.28). Here, the pair is made up by one electron from each atom to form a stable outer shell for each. The resulting compound, hydrogen chloride (HCl) is depicted by: H – Cl

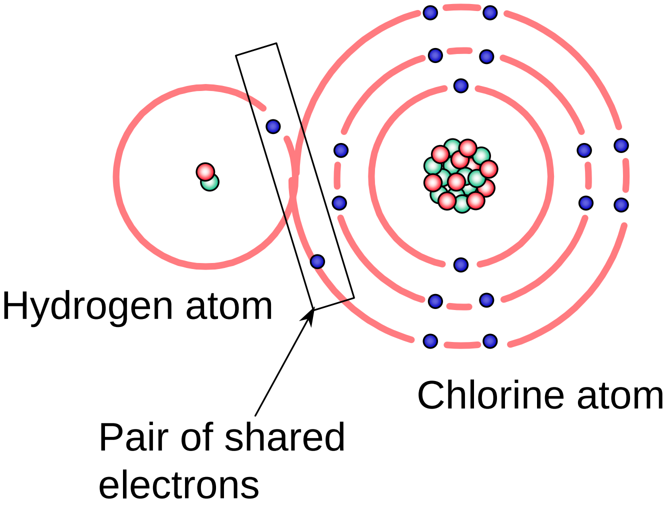


Figure 1.28
Single-pair covalent bond formed from hydrogen and chlorine

More than one pair of electrons can form a covalent bond. An oxygen molecule, for example, (with six valence electrons) is formed when two pairs of electrons are shared – again resulting in a stable outer shell of eight electrons for each atom. Here, the double pair is represented by a double dash (=):

O = O

In the case of nitrogen, with five valence electrons, a molecule is formed by a triple bond in which three pairs of electrons (three electrons from each atom) give rise to a stable outer shell for each atom. Here, the triple pair is represented by a triple dash (≡):

N ≡ N

Chemical formulae

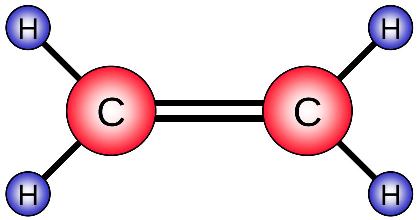
The most commonly used chemical formula is the ***molecular formula***, which gives the actual composition of a molecule. The molecular formula H_2O, for example, indicates that a water molecule comprises two H atoms and one O atom. Similarly, the formula for ethene is C_2H_4 — indicating that an ethene molecule is made up of two carbon atoms and four hydrogen atoms.

At this point a distinction needs to be drawn between the molecular formula, stated above, and what is termed an ***empirical formula***.

Whilst the molecular formula gives the composition of a molecule, the empirical formula expresses the composition of a substance in terms of whole-number ratios.

Figure 1.29 shows the structure of an ethene molecule. The empirical formula would be written CH_2 — indicating the *ratio* of atoms i.e. there are two hydrogen atoms for each carbon atom. The molecular formula, on the other hand (written C_2H_4), indicates that a molecule of ethene comprises two carbon atoms and four hydrogen atoms.

For even more information the ***shortened structural*** formula is used. This shows the sequence of groups or atoms in a molecule. And for more information still, the ***full structural*** or ***displayed*** formula shows all the bonds (both single and double) that make up the molecule.



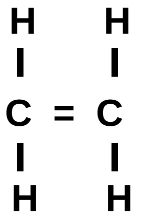
Ethene molecule

Empirical formula: CH_2

Molecular formula: C_2H_4

Shortened structural formula: $CH_2 = CH_2$

Displayed formula:



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

Figure 1.29
Empirical, molecular and displayed, formulae for ethene

It should be noted that in organic chemistry, even more information than that provided by the displayed formula is required. For example, ***isomers*** are compounds having the same molecular formula but different arrangements of atoms in their molecules.

Often, such compounds can only be distinguished from each other using ***stereochemical formulae*** that show the structure of the molecule in 3-D.

Thus, whilst the molecular formula for butene is C_4H_8 it has two different stereochemical formulae (Figure 1.30).

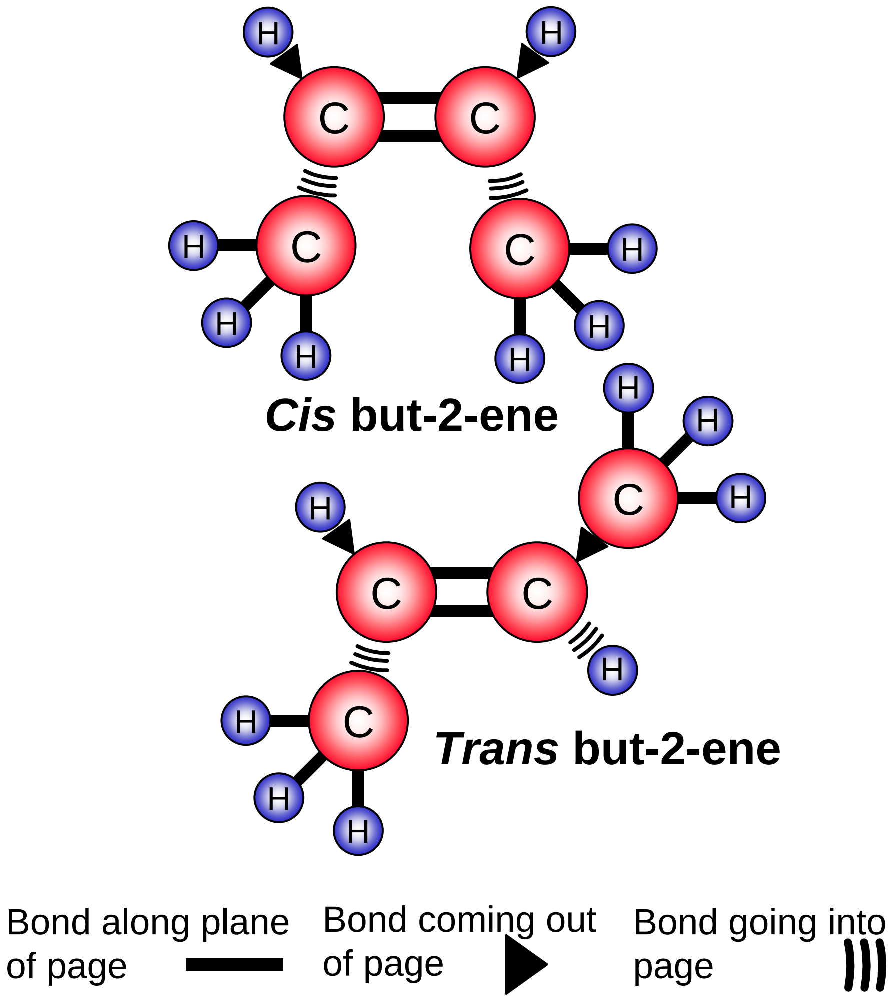


Figure 1.30
Stereochemical formulae illustrates the difference in the molecular formula for butene

We have already seen how some elements such as oxygen and nitrogen occur as simple molecules even when not combined with other elements. These give the formula O_2 and N_2 respectively.

1.7 Chemical equations

A chemical equation gives a ‘before and after’ picture of a chemical reaction.

In its most basic form, it may be written out:
Sodium + Water → Sodium hydroxide + Hydrogen

The two substances that produce the reaction, and are called ***reactants***, are written on the left hand side of the equation and the result or products of the reaction are written on the right hand side. The + sign stands for ‘react with’ and the arrow (→) stands for ‘reacts to yield’. Thus, the above equation indicates that sodium reacts with water to yield sodium hydroxide and hydrogen.

In practice, the names of the materials involved in the reaction are not written out in full but are replaced by their chemical formulae:

$Na + H_2O \rightarrow NaOH + H_2$

Whilst this equation shows the reaction that takes place, it does not convey the complete picture since closer examination shows that it is chemically unbalanced — i.e. the number of atoms on the one side is not the same as the other (Table 1.2).

Table 1.2
Atoms in formula do not balance

Formula	**Na**	**+**	**H_2 O**	**→**	**Na O H**	**+**	**H_2**
Number of atoms	1		2 1		1 1 1		2
Totals	4			≠	5		

In order to balance the equation it may be rewritten as shown with the number in front of each equation, called the coefficient, indicating the number of atoms :

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

Now, an audit, as shown in Table 1.3, show that there is a balance.

Table 1.3
Atoms in formula now balance

Formula	**2(Na)**	**+**	**2(H_2 O)**	**→**	**2(Na O H)**	**+**	**H_2**
Number of atoms	2(1) 2		2(3) 6		2(3) 6		2 2
Totals	8			=	8		

The equation may be extended even further by including what are termed state symbols after each formula that indicate the physical state of each molecule. The state symbols (written in brackets) are:

(s) = solid
(l) = liquid
(aq) = aqueous (solution in water)
(g) = gas

Thus, the sodium reaction with water would be:

$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2\,(g)$

Finally, when studying electrolytes in solution, the chemical properties are best represented by an ionic equation which is only concerned with the ions of the participant substances in the reaction.

Thus the reaction:

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

may be rewritten:

$Na^+OH^-(aq) + H^+Cl^-(aq) \rightarrow Na^+Cl^-(aq) + H_2O(l)$

Here, Na^+, OH^- , Cl^- and H^+ are all ions. Since Na^+ and Cl^- appear on both sides of the equation, they are uninvolved the ionic reaction and are thus omitted. Now the ionic equation is simply:

$\cancel{Na}^+OH^-(aq) + H^+\cancel{Cl}^-(aq) \rightarrow \cancel{Na}^+\cancel{Cl}^-(aq) + H_2O(l)$

$OH^-(aq) + H^+\,(aq) \rightarrow H_2O(l)$

1.8 Naming compounds

Many compounds have *trivial* names —names that give little information about the structure of the compound. These include names such as salt (NaCl), borax ($Na_2B_4O_7{\cdot}10H_2O$), chalk ($CaCO_3$), or even proprietary names such as Teflon ($F(CF_2)_nF$). In addition, there are other chemical compounds whose names are universally associated with a chemical formula (e.g. water (H_2O)). However, most of these names are often difficult to interpret. As a result, most compounds are named using a systematic internationally agreed system.

The compounds of metals and non-metals containing, for example, two different elements are named by first taking the name of the metallic element followed by the *main* part of the name of the non-metal, which is then modified with the suffix ***-ide***. Thus, the compound of sodium and chlorine takes the metallic element first (sodium) followed by the modified form of chlorine (chloride): i.e. sodium chloride (NaCl).

Other such compounds include:
CaS — calcium sulfide;
MgO — magnesium oxide;
SiN — silicon nitride; and
ZnS — zinc sulfide

When more than two atoms are involved use can be made of a prefix:

mono-	1	hexa-	6
di-	2	hepta-	7
tri-	3	octa-	8
tetra-	4	nona-	9
penta-	5	deca-	10

Thus we get:
CO — carbon monoxide;
CO_2 — carbon dioxide
NO_2 —nitrogen dioxide;
CS_2 — carbon disulfide;
SF_6 — sulfur hexafluoride;
$GeCl_4$ — germanium tetrachloride; and
N_2O_4 — dinitrogen tetraoxide.

Another frequently used suffix is ***-ate*** which usually indicates the presence of oxygen. Thus: nitrate, NO^{3-}; sulfate, SO_4^{2-}; and phosphate, PO_4^{3-} .

The suffix ***-ite*** indicates fewer oxygen atoms than in the corresponding -*ate* ion, with the prefix *hypo*- used with the suffix -*ite* indicating still fewer. The prefix *per*- indicates more oxygen, or less negative charge, than the corresponding -ate ion. Thus:

Chlorate	ClO_3^-
Chlorite	ClO_2^-
Hypochlorite	ClO^-
Perchlorate	ClO_4^-

Certain metals can be found in more than one ionic state. Iron, for example, occurs as either Fe^{2+} or Fe^{3+}. In such cases, the suffix -*ous* may be used to identify the lower state and -*ic* the higher state. Thus:
Fe^{2+} = ferrous ion
Fe^{3+} = ferric ion
Cu^+ = cuprous ion
Cu^{2+} = cupric ion

This system of denoting the lower and higher valency states of metal cations has, however, given way to the Stock System in which the oxidation number of the metallic element is indicated by Roman numbers in parenthesis placed immediately after the atom concerned.

The $FeCl_2$ is denoted Iron (II) chloride rather than ferrous chloride and $FeCl_3$ is denoted Iron (III) chloride rather than ferric chloride.

1.9 Atomic weight

Although it is customary to use the term 'atomic weight', the term 'atomic mass' is more appropriate. Whilst weight is the force exerted on the body by the influence of gravity, mass is a measure of the quantity of matter in a body independent of gravity.

Historically, oxygen was taken as a standard of mass measurement and the oxygen atom was assigned a value of 16.0000 ***atomic mass units*** (amu). On this basis, helium was found to have an atomic weight of 4.003 amu, fluorine 19.000, and sodium 22.997.

However, since the early 1960s, the isotope carbon-12 has been used as a standard and the amu is now defined as being 1/12th of an atom of carbon-12 in which:

1 amu = $1.6605665 \times 10^{-24}$ g

In reality the atomic weights based on carbon-12 are in close agreement with those based on natural oxygen.

Table 1.4 compares the atomic weights of the three subatomic particles which show that the atomic weight of the electron is nearly 4000 times less than that of the nucleus and can thus be ignored. In addition, the proton and neutron both have masses close to unity. Since the atomic number is defined as the number of protons in the nucleus, we would expect that the atomic weight would be just over twice that of the atomic number.

Table 1.4
Atomic weights of the three subatomic particles

Particle	Atomic weight (amu)
Proton	1.007276
Neutron	1.008665
Electron	0.0005486
Total	**2.0164896**

This, in fact, is shown in Table 1.5 which lists the atomic weights of various elements together with their atomic numbers.

Table 1.5
The atomic weights of various elements together with their atomic numbers.

Element	Symbol	Atomic weight (amu)	Atomic number
Hydrogen	H	1.008	1
Helium	He	4.003	2
Carbon	C	12.01	6
Oxygen	O	16	8
Sodium	Na	22.99	11
Chlorine	Cl	35.45	17
Nickel	Ni	58.7	28
Germanium	Ge	72.59	32
Platinum	Pt	195.1	78
Gold	Au	197	79
Uranium	U	238	92

How about the mass of a molecule?

In fact it's really quite simple. The ***molecular weight*** or mass is merely the sum of the atomic weights of each element.

Thus, the molecular weight of water (H_2O) would be the sum of the atomic weights of the two hydrogen atoms (1 + 1) and one oxygen atom i.e. 1 + 1+ 16 = 18.

Because there are many substances that do not, in fact, comprise molecules (e.g. salts such as sodium chloride) the term ***formula weight*** is often used in place of molecular weight and is calculated in exactly the same way. Thus, the formula weight of sodium chloride (NaCl) would be the sum of the atomic weights of sodium (22.99) and chlorine (35.45) i.e. 22.99 + 35.45 = 58.44.

We saw earlier that an 'atomic mass unit' (amu) was defined as having a mass of:
$1 \text{ amu} = 1.6605665 \times 10^{-24} \text{ g}$

Alternatively we could say that there were:
$6.022 \times 10^{23} \text{ amu} = 1\text{g}$

The figure of 6.022×10^{23} is referred to as ***Avogadro's number*** and is termed a ***mole*** and is given the symbol ***mol***. A mole is a measure of the amount of a substance and 1 mol of any substance contains 6.022×10^{23} molecules or atoms.

The formal SI definition of a mole is:

> "… the amount of any substance that contains as many particles as there are atoms in 12 g of carbon-12. When the mole is used the particles (atoms, molecules, ions, electrons, etc.) must be stated."

Thus:
One mole of carbon-12 *atoms* thus has a mass of 12 g.
One mole of oxygen *atoms* has a mass of 16 g.
One mole of oxygen *molecules* has a mass of 32 g.

1.10 Molar concentrations

Many chemical reactions are carried out in solution and the concentration is usually defined in terms of the number of moles of the substance (the solute) contained in 1 ℓ of solution. This is called its molar concentration or molarity.

For example, if 10 g of NaCl is dissolved in distilled water to give 1 ℓ of the solution, what is the solution molarity?

We have already determined that the formula weight of NaCl = 58.44 and thus, by definition:
58.44 g of NaCl = 1 mol
Then:
10 g of NaCl = 0.171 mol

This is the thus the amount of NaCl dissolved in 1 ℓ of the solution and the molarity is 0.171 mol/ℓ.

1.10.1 Acids and bases

Whilst in a purely covalent bond the electrons are shared symmetrically, in most cases the shared electrons tend to be closer to one atom's nucleus that the other. Such bonds have a partial ionic character in which one part of the molecule has a net positive charge and the other a net negative charge. These molecules are said to be polar.

Figure 1.31 shows a molecule of water in which the shared electrons are more likely to be found around the oxygen atom. The result is that there is a net negative charge on the oxygen atom. And since the electrons spend less time orbiting the hydrogen atoms there is a net positive charge on each hydrogen atom.

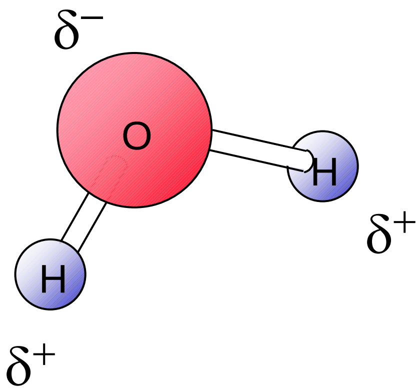


Figure 1.31
In a water molecule the shared electrons are more likely to be found around the oxygen atom

It should be noted that, as distinct from ionic bonding, the net charges are less than 1+ or 1-, this being indicated by the symbol (δ).

In pure water, a small number of molecules ionise — each forming a hydrogen ion (H^+) and a hydroxide ion (OH^-). This reaction is called ***self-ionisation***. Since the number of hydrogen and hydroxide ions is equal, the water is neutral. However, this balance can be upset by a number of compounds that dissolve or react with the water and produce either hydrogen ions or hydroxide ions.

Substances that react in this manner and produce hydrogen ions (H^+) in the solution are called ***acids*** and those that react and produce hydroxide ions are called ***bases***.

Another name used to describe the hydrogen ion (H^+) is ***proton*** and thus acids may also be described as proton donors and bases as proton acceptors.

In reality, the hydrogen ions do not exist on their own but are attached to the water molecules to become what are called hydroxonium ions (H_3O^+). This is shown in the reaction of hydrochloric acid (HCl) with water:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Nevertheless, because only the hydrogen ion takes part in the reaction in a solution, the H+ ions may be considered as the active ingredient and, for all intents and purposes, the hydroxonium ion may be considered to be a hydrogen ion.

A base has been described as a substance that gives hydroxide ions (OH^-) when reacting or dissolving in water. Alternatively, it has been described as a proton acceptor. A base is, therefore, the chemical opposite to an acid. As a result, a base may be further described as a substance that will neutralise an acid by accepting its hydrogen ions.

Thus, in the right proportions, the reaction of hydrochloric acid (HCl) with sodium hydroxide (NaOH) gives:

$$HCl + NaOH \rightarrow H_2O + NaCl$$

resulting in a solution containing ordinary table salt.

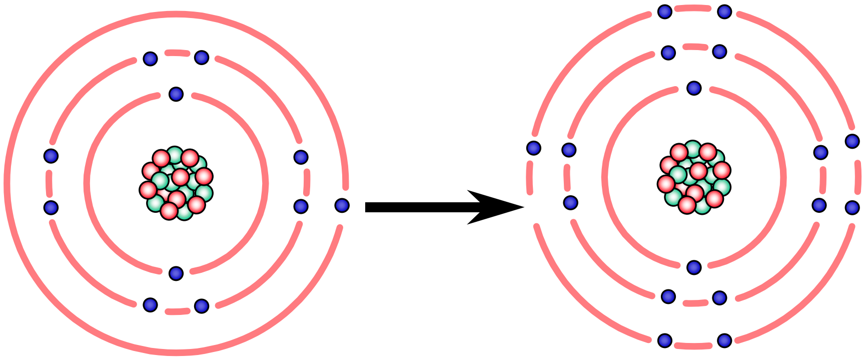
When a base is dissolved in water the resulting solution contains more hydroxide ions than hydrogen ions and is termed an ***alkaline***. The determination of whether a solution is acidic or alkaline, and their relative strengths, is compared on a pH scale.

1.11 Oxidation-reduction

In our discussions on bonding, we saw how both ionic and covalent bonding involved a shift in electron density from one atom to another.

In the case of sodium chloride (NaCl), for example, an electron was transferred completely from Na to Cl to form the Na^+ and Cl^- ions (Figure 1.32). This shift in electron density, from one atom to another, is termed an ***oxidation-reduction*** reaction — usually shortened to ***Redox*** reaction.

Oxidation refers to the *loss* of electrons during a reaction whilst ***reduction*** refers to the *gain* of electrons. Oxidation and reduction always occur together — with one substance accepting the electrons that another loses. Thus in the reaction of sodium chloride, sodium loses an electron and is therefore oxidised whilst the chlorine atom gains an electron and is said to be reduced.



Sodium atom *loses* an electron and is therefore **oxidised**
Sodium acts as the **reducing agent**

Chlorine atom *gains* an electron and is therefore **reduced**
Chlorine acts as the **oxidising agent**

Figure 1.32
Loss of electrons is called oxidation and gain of electrons is termed reduction

Although in the sodium chloride reaction, the sodium supplies the electron, and is thus oxidised, it acts as the reducing agent. Likewise the chlorine, which is reduced, acts as the oxidising agent.

A measure of the power of a substance to gain electrons is called the Redox potential. A reducing agent that readily loses electrons will have a negative potential whilst oxidising agents will have a positive potential.

2

Electrochemical Cells

Objectives

When you have completed this chapter you should be able to:

- Describe the basic principle of the electrochemical cell
- Show how a potential difference is formed between two dissimilar electrodes immersed in water
- Demonstrate how a simple voltaic cell is formed
- Explain how a Daniell cell works
- Understand the use of an electrolytic bridge
- Discuss the importance of the electrochemical series and how it is applied

2.1 Introduction

If a metallic rod such as zinc is placed in water, there is a tendency for a redistribution of electric charges to take place.

Firstly, the water molecules attract positive ions from the metal. Countering this, however, is the fact that as the positive ions leave the metal, the rod has a tendency to become negatively charged. This results in the positive ions being held to the surface of the rod — with the ions thus being said to be ***adsorbed*** onto the surface of the metal (Figure 2.1).

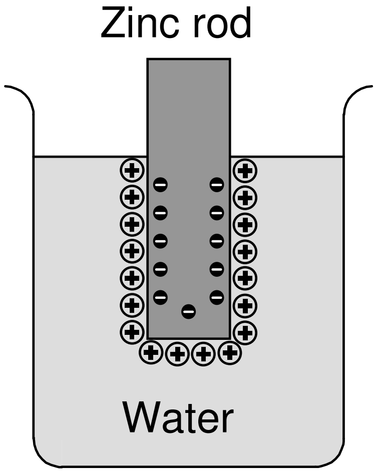


Figure 2.1
When a zinc rod is placed in water, positive ions are adsorbed onto its surface and the rod will have a negative charge

Some of the adsorbed ions may break away from the surface of the metal and the rod will actually lose mass (Figure 2.2). However, because each ion that is lost causes the rod to become more negatively charged this reaction, called desorption, can only happen to a few ions before an equilibrium is rapidly reached.

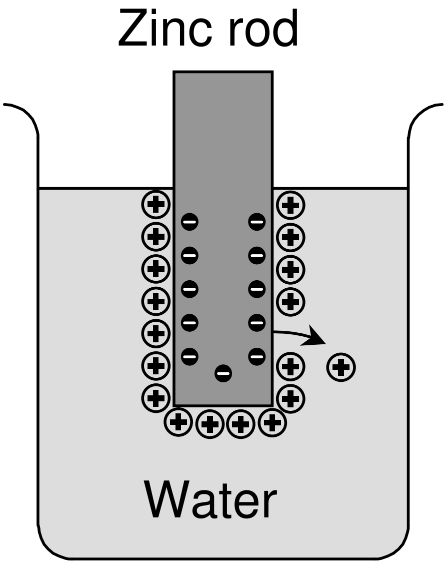


Figure 2.2
Some of the adsorbed ions break away from the surface of the zinc and it loses mass

The amount of negative charge on such a metal rod placed in water is determined largely by the reactivity of the metal. Zinc atoms ionise easily and thus the negative charge will be relatively high — with a potential difference thus existing across the zinc/solution junction. However, copper atoms, for example, ionise only with some difficulty and thus, as shown in Figure 2.3, the amount of negative charge is considerably less. The result is that the potential difference across the copper/solution junction is also considerably less.

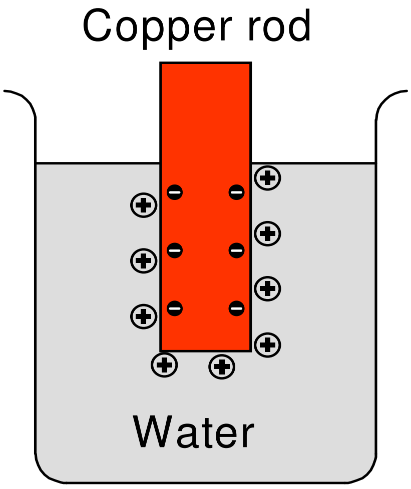


Figure 2.3
A copper rod placed in water will have fewer positive ions adsorbed onto its surface and the rod will have a smaller negative charge

2.2 Potential difference

Assume now that a zinc rod and a copper rod, referred to as ***electrodes***, are both placed in water and a high impedance voltmeter is connected across them (Figure 2.4). As a result of their different electrode potentials, the voltmeter would indicate that a potential difference now exists, between the copper and zinc electrodes, of about 1.1 V.

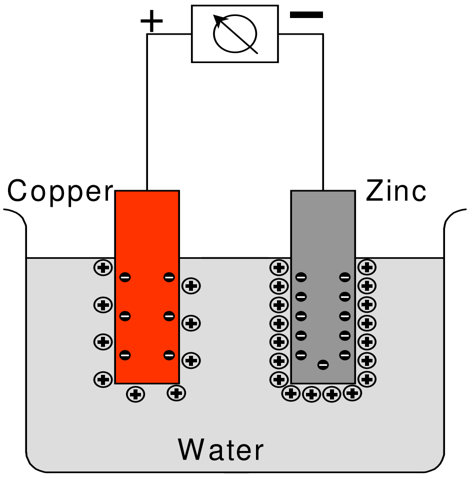


Figure 2.4

A high impedance voltmeter connected across the electrodes shows a potential difference between them of about 1.1 V

If, instead of the high impedance voltmeter, a conducting wire is connected across the electrodes there will be an initial brief flow of electrons from the zinc electrode to the copper electrode (Figure 2.5). Since the zinc electrode loses electrons it will become less negatively charged whilst the copper electrode will gain electrons and will become more negatively charged.

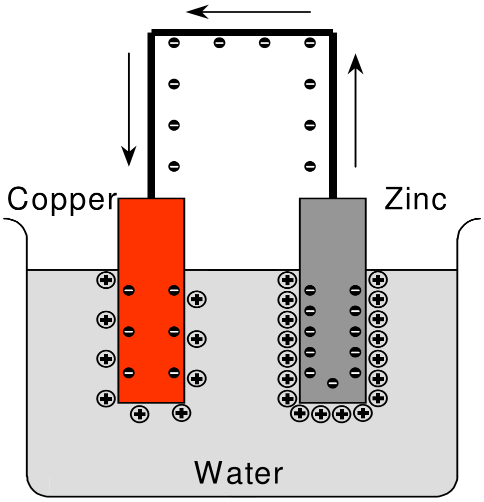


Figure 2.5

If the electrodes are connected using a conducting wire there will be a brief flow of electrons from the zinc electrode to the copper electrode and the zinc electrode will be less negatively charged and the copper electrode will be more negatively charged

The reduced negative charge of the zinc electrode means that the adsorbed positive ions are now less strongly attached to its surface and may become detached — exposing new atoms. Since this encourages more ionisation, the zinc electrode will again tend to become more negative.

At the copper electrode, the inflow of electrons attract adsorbed copper ions even more and further ionisation is thus discouraged, As a result, both electrodes end up at the same potential and no potential difference will now exist across them (Figure 2.6).

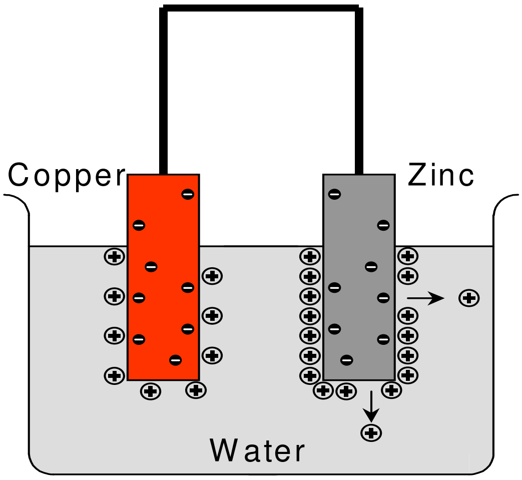


Figure 2.6
After as short time both electrodes end up at the same potential and no potential difference will exist across them

2.3 Simple voltaic cell

One means of overcoming this stalemate is to make the solution acidic (e.g. a dilute solution of sulphuric acid) and thus increase the number of free hydrogen ions (H^+) in the solution. As before, ions will continue to leave the zinc electrode — with ionisation still taking place and the excess electrons being conducted through to the copper electrode.

Now, at the copper electrode, the inflow of electrons attracts the positive hydrogen ions, which are adsorbed onto the electrode's surface and then combine with the electrons to form hydrogen gas, which bubbles to the surface (Figure 2.7). In this manner, a current will continue to flow through the conductor until either the zinc electrode has been completely corroded away or until all the hydrogen ions in the solution (called the ***electrolyte***) have been released as gas at the copper electrode.

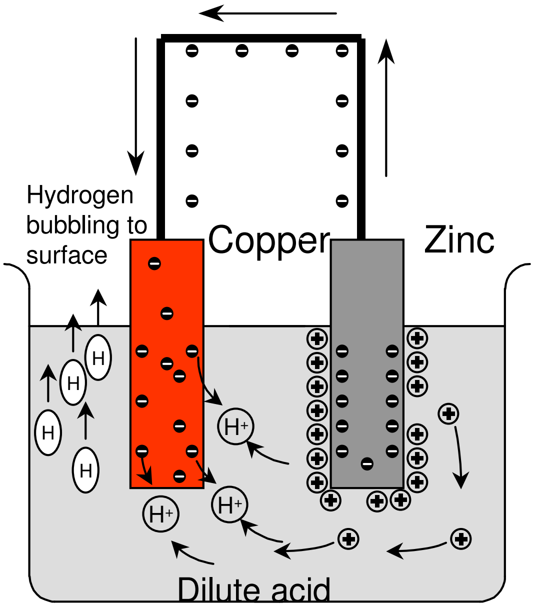


Figure 2.7
By making the electrolyte acidic, the inflow of electrons on the copper electrode attracts the positive hydrogen ions which are adsorbed onto the electrode's surface and combine with the electrons to form hydrogen gas

One of the major defects of this simple voltaic cell is that the liberated hydrogen forms a layer on the copper electrode (Figure 2.7). Apart from considerably increasing the internal resistance of the cell, the copper/solution junction now becomes a copper/hydrogen junction that produces an emf that is in opposition to that produced by the current flow. The result is that on connecting the two electrodes via the conductor to produce a current flow, within a very short time, the emf across the electrodes will fall from about 1.1 V to 0.7 V or even less. This effect is termed ***polarisation***.

2.3.1 The Daniell cell

One method of overcoming this problem is by means of the Daniell cell shown in Figure 2.8 — a modified form of the simple voltaic cell. Here the zinc electrode is again placed in a dilute solution of sulphuric acid (or, more traditionally, zinc sulphate). The difference is that in this case the copper electrode is effectively immersed in a saturated solution of copper sulphate which acts as the depolariser.

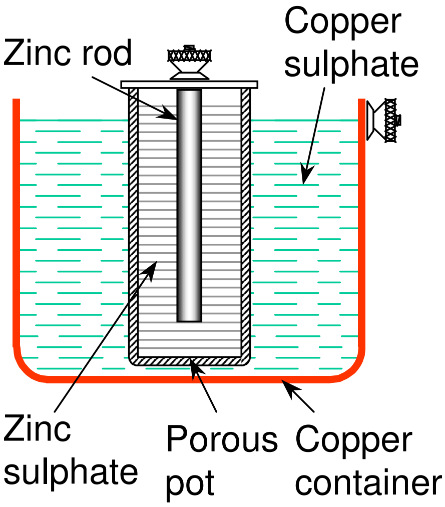


Figure 2.8
The Daniell cell — a modified form of the simple voltaic cell —overcomes the problem of polarisation

The cell is redrawn in Figure 2.9 to illustrate the action which shows that, in effect, we now have two ***half-cells*** — the zinc electrode in the sulphuric acid forming one half-cell and the copper electrode in the copper sulphate forming the other half-cell. Earlier we had seen how the positive hydrogen ions of the sulphuric acid were used to attract the excess electrons in the copper electrode. In this case, the Cu^{2+} cations of the copper sulphate ($Cu^{2+}SO_4$) are used to attract the excess of electrons in the copper electrode — with the ions thus deposited as metallic copper on the electrode.

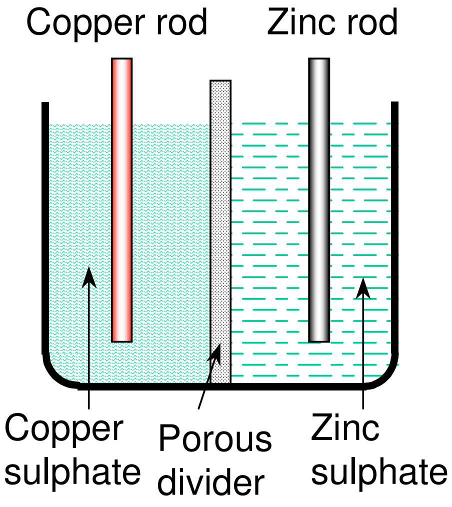


Figure 2.9
In effect, the Daniell cell comprises two half-cells — the zinc electrode in the zinc sulphate forming one half-cell and the copper electrode in the copper sulphate forming the other half-cell

2.4 Electrolytic bridge

The two half-cells are connected ‘electrically’ by the porous pot which prevents any rapid mixing of the two electrolytes but at the same time allows ions to diffuse through it.

If the two solutions were not in contact in this way (Figure 2.10) the electrode reactions would rapidly cease. Zinc cations (Zn^{2+}) leaving the zinc electrode would rapidly build up a positive charge in the electrolyte and ultimately prevent electrons leaving the zinc electrode. Similarly, the adsorption of copper ions on the copper electrode would leave the solution with an overall negative charge (SO_4^{2-}) that would prevent negative electrons entering the copper electrodes.

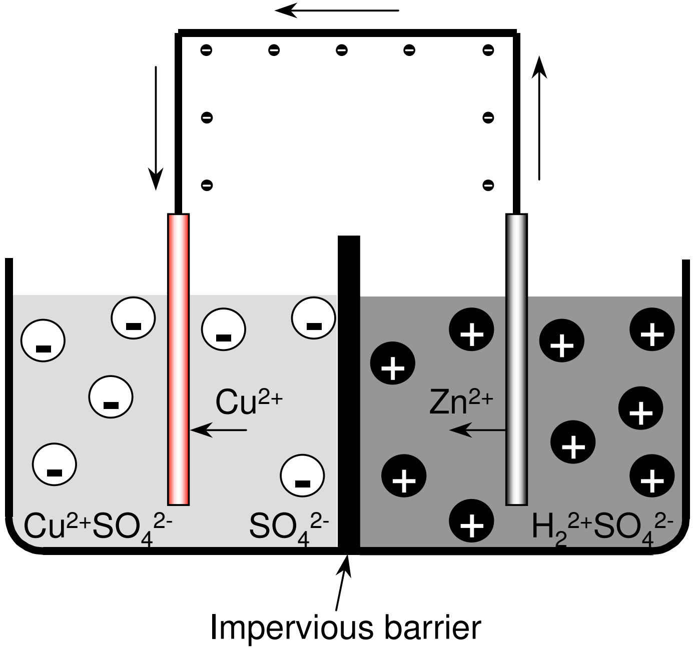


Figure 2.10
With the two solutions separated by an impervious barrier, zinc cations (Zn^{2+}) leaving the zinc electrode would build up a positive charge in the electrolyte and thus prevent electrons leaving the zinc electrode. Similarly, the copper electrode would leave its electrolyte with an overall negative charge (SO_4^{2-}) that would prevent negative electrons entering the copper electrodes

The effect of the porous barrier (Figure 2.11) is thus to allow the negative sulphate anions (SO_4^{2-}) to pass through the barrier and neutralise the positive zinc cations (Zn^{2+}), and vice versa, so that both the solutions would remain neutral.

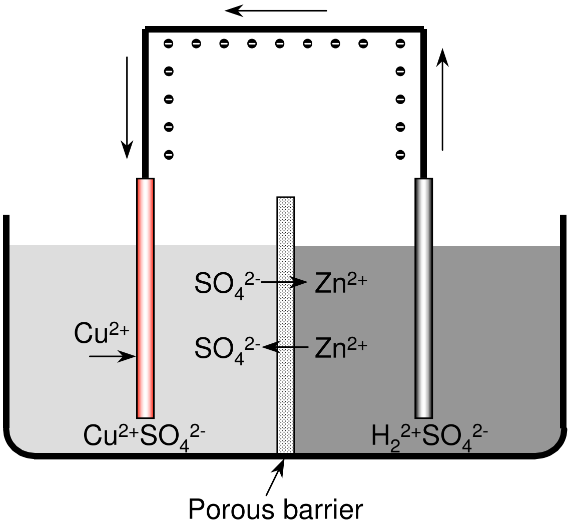


Figure 2. 11
The porous barrier allows the negative sulphate anions (SO_4^{2-}) to pass through the barrier and neutralise the positive zinc cations (Zn^{2+}), and vice versa, so that both solutions remain neutral

One of the problems of such a simple porous clay barrier is the fact that different rates of diffusions of the cations and anions can occur across the barrier — giving rise to a liquid junction potential.

This effect can be considerably reduced by using an alternative method of connecting the two half-cells by means of what is termed a ***salt bridge*** (Figure 2.12). In this example the salt bridge comprises a glass tube filled with an electrolyte (usually potassium chloride (KCl) or potassium nitrate (KNO_3)) with porous plugs at either end.

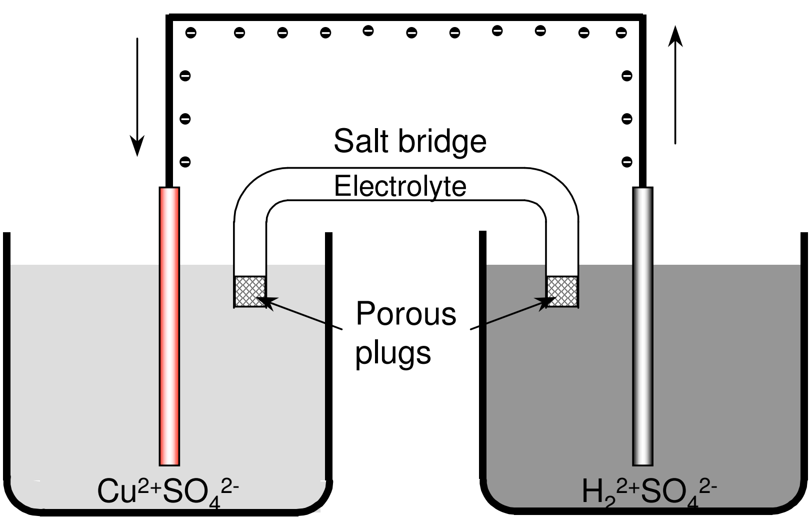


Figure 2.12
A salt bridge, comprising a glass tube filled with an electrolyte and sealed with porous plugs at either end, can reduce the liquid junction potential

These salts produce ions with approximately equal diffusion rates, with either negative anions diffusing from the salt bridge into the copper half-cell or Cu^{2+} cations diffusing into the salt bridge.

2.5 Electrochemical series

The measured potential for a given cell reaction is dependent on the concentration of the ions, the temperature, and the partial pressure of any gases involved in the reaction.

Earlier we saw that it is impossible to measure the potential associated with an individual half-cell and that a potential difference can only be measured when the two half-cells are connected.

In practice the hydrogen electrode is not easy to use as a general standard and is often replaced by the ***calomel*** (mercury chloride) electrode, whose potential is defined in terms of the hydrogen electrode.

Despite the fact that the potential of an isolated half-cell cannot be measured, values have been determined by comparing a range of half-cell reactions with that of an arbitrary reference electrode — a ***hydrogen electrode*** — which has been assigned an ***electrode potential*** or what is termed a ***standard reduction potential*** of 0.00 V.

Figure 2.13 shows the standard reduction potentials (otherwise known as the electrochemical series) for a number of half reactions at a fixed temperature of 25°C, a fixed pressure of 1 bar, and a fixed ion concentration of 1 mol/ℓ.

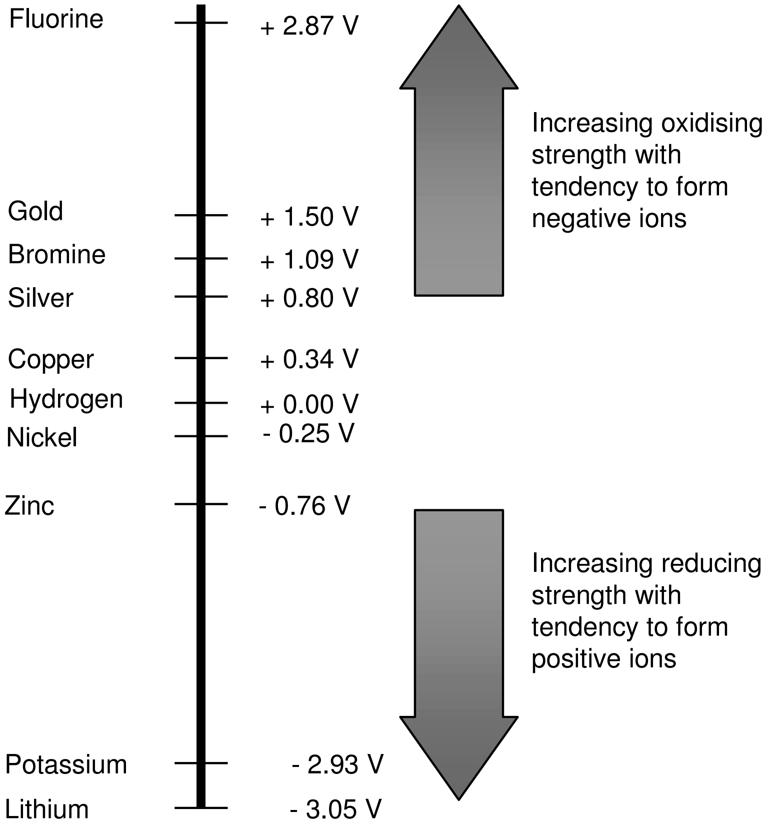

Fluorine
+ 2.87 V
Gold
+ 1.50 V
Bromine
+ 1.09 V
Silver
+ 0.80 V
Copper
+ 0.34 V
Hydrogen
+ 0.00 V
Nickel
- 0.25 V
Zinc
- 0.76 V
Potassium
- 2.93 V
Lithium
- 3.05 V
Increasing oxidising strength with tendency to form negative ions
Increasing reducing strength with tendency to form positive ions

Figure 2.13
Electrochemical series for a number of elements

Since the measured cell potential represents the difference between the reduction potential of one half-cell and the reduction potential of the other, this series now enables us to determine the ***standard cell potential*** (E^0_{cell}) for any cell from:

E^0_{cell} = [Potential of reduced substance] - [Potential of oxidised substance]

Thus, for a zinc/copper cell the standard cell potential would be given by:

E^0_{cell} = [+0.34] - [-0.76] = 1.1 V

and for a silver/copper cell:

E^0_{cell} = [+0.8] - [+0.34] = 0.46 V.

In the calculations given above, no account has been taken of temperature or the ionic concentration as these were assumed to be fixed at 25°C and 1 mol/ℓ respectively.

The relationship between the cell potential and the concentrations of the reactants are accounted for in the ***Nernst equation*** which states:

$$E = E^o_{cell} - \frac{RT}{nF} \ln \frac{1}{a_i}$$

where:

E = total potential (in millivolts) between two electrodes
E^o_{cell} = standard cell potential
R = universal gas constant (Joules/mol-Kelvin)
T = absolute temperature (Kelvin)
n = charge of the ion
F = Faraday constant (Coulombs/mol)

a_i = activity of the ion

The significance of this equation is that if all the other factors were held constant, then the emf of the cell will vary according to the ion activity and, therefore, according to its concentration.

Further, if the electrode were made sensitive only to the H^+ ions, the emf of the cell would indicate the acidity /alkalinity of the medium.

3

pH Measurement

Objectives

When you have completed this chapter you should be able to:

- Show the need for pH measurement
- Describe the properties of water
- Define pH
- Demonstrate the principle of both the measuring and reference electrodes and their relationship to each other
- Understand the Nernst equation and its dependence on temperature
- List the various sources of error in the measurement of pH
- Show how calibration is carried out

3.1 Introduction

The measurement of pH is one of the oldest chemical analysis methods in the world. Using our sense of taste most people can easily determine that orange juice is more acidic than milk and the 'cola' based beverages are even more acidic still. Interestingly, what is regarded as 'good tasting food' is acidic in nature (Figure 3.1).

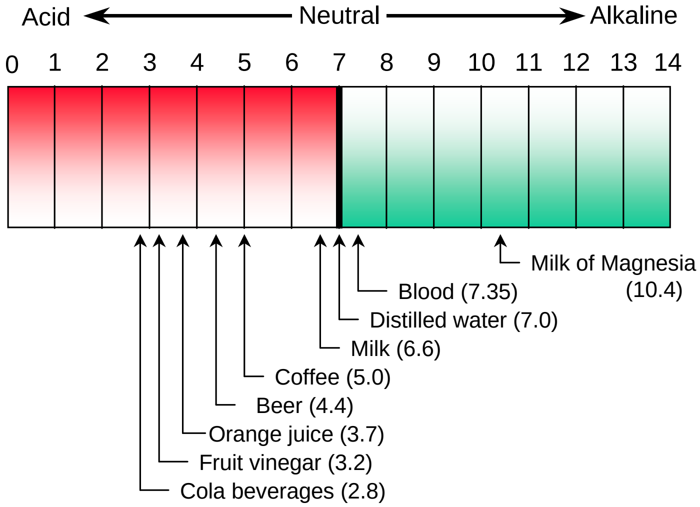

Acid
Neutral
Alkaline
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Milk of Magnesia (10.4)
Blood (7.35)
Distilled water (7.0)
Milk (6.6)
Coffee (5.0)
Beer (4.4)
Orange juice (3.7)
Fruit vinegar (3.2)
Cola beverages (2.8)

Figure 3.1
The pH values for a range of commonly encountered products

In industrial processes the measurement and control of the acidity/alkalinity levels of process media is becoming increasingly more important. Application areas include: neutralisation of effluent in steel, pulp and paper, chemical and pharmaceutical manufacturing; cooling tower control; maximising efficiency in plating and surface treatment; control of municipal drinking water and wastewater purification plants; and quality control in the food and beverage industries.

In its simplest definition, pH could be defined as a measure of the acidity or alkalinity of a solution. However, whilst a 5% solution of boric acid can be used as an eye wash, the use of a 5% solution of sulphuric acid would be disastrous. Thus the knowledge of only the concentration of an acid or base is of little practical use.

One of the most important identifying factors of an acid or base is the hydrogen activity. Both boric acid ($B(OH)_3$) and sulphuric acid (H_2SO_4) contain hydrogen. However, whilst the hydrogen in sulphuric acid dissociates in the presence of water to become free hydrogen ions, very little of the hydrogen in boric acid is released as free hydrogen ions. Thus, the true measure of acidity (or alkalinity) concerns the measurement of the dissociated or free hydrogen ion concentration of a given solution.

3.2 Properties of water

Earlier we saw that even pure water ionises into an equal number of hydrogen (H^+) and hydroxide (OH^-) ions. This self-ionisation is very small and at 25°C the molar concentration of each is only 1.10^{-7} mol/ℓ .

In all other aqueous solutions, the relative concentrations of each of these ions are unequal such that as one increases the other decreases to form a constant.

This relationship may be expressed as:

$$[H^+] \times [OH^-] = 1 \times 10^{-14} = K_w$$

in which K_w is referred to as the ***ion-product constant for water***.

In essence this shows that the product of hydrogen and hydroxide ions is equal to 1×10^{-14} $(mol/\ell)^2$. Therefore, if the concentration of one increases by a factor of 10, the other decreases by a factor of 10.

In an aqueous solution where the hydrogen concentration is greater than 10^{-7} the solution is acid and if less than 10^{-7} the solution is alkaline.

3.3 Definition of pH

pH is derived from the initial letter of the French word ‘potenz’ meaning power and thus expresses the ***power of hydrogen***. pH is actually defined as the negative logarithm of the hydrogen ion concentration and is expressed mathematically as:

$$pH = -Log [H^+]$$

where:
$[H^+]$ is hydrogen ion concentration in mol/ℓ.

This value ranges from 0 to 14 pH — with values below 7 pH exhibiting acidic properties (an increase in hydrogen ions) and values above 7 pH exhibiting alkaline properties (an increase in hydroxide ions).

Since the pH value is an expression of the ratio of $[H^+]$ to $[OH^-]$ concentration, then at 7 pH, the ratio of $[H^+]$ to $[OH^-]$ is equal and the solution is neutral. Because the pH equation is logarithmic, a change of one pH unit represents a 10 fold change in concentration of hydrogen ions. Table 3.1 illustrates the relationship between pH and the H^+ and OH^- concentrations.

Table 3.1

pH values compared with the hydrogen/hydroxide concentrations

$[OH^-]$ concentration (mol/ℓ)		pH	$[H^+]$ concentration (mol/ℓ)		
1×10^{-14}	0.00000000000001	0	1	1×10^{0}	
1×10^{-13}	0.0000000000001	1	0.1	1×10^{-1}	
1×10^{-12}	0.000000000001	2	0.01	1×10^{-2}	Increasing acidity
1×10^{-11}	0.00000000001	3	0.001	1×10^{-3}	
1×10^{-10}	0.0000000001	4	0.0001	1×10^{-4}	
1×10^{-9}	0.000000001	5	0.00001	1×10^{-5}	
1×10^{-8}	0.00000001	6	0.000001	1×10^{-6}	Neutral
1×10^{-7}	0.0000001	7	0.0000001	1×10^{-7}	
1×10^{-6}	0.000001	8	0.00000001	1×10^{-8}	
1×10^{-5}	0.00001	9	0.000000001	1×10^{-9}	
1×10^{-4}	0.0001	10	0.0000000001	1×10^{-10}	Increasing alkalinity
1×10^{-3}	0.001	11	0.00000000001	1×10^{-11}	
1×10^{-2}	0.01	12	0.000000000001	1×10^{-12}	
1×10^{-1}	0.1	13	0.0000000000001	1×10^{-13}	
1×10^{0}	1	14	0.00000000000001	1×10^{-14}	

In the former examples, a 5% sulphuric acid solution will have a pH of approximately 0.3 and the 5% boric acid solution will have a pH of about 5 (Figure 3.2).

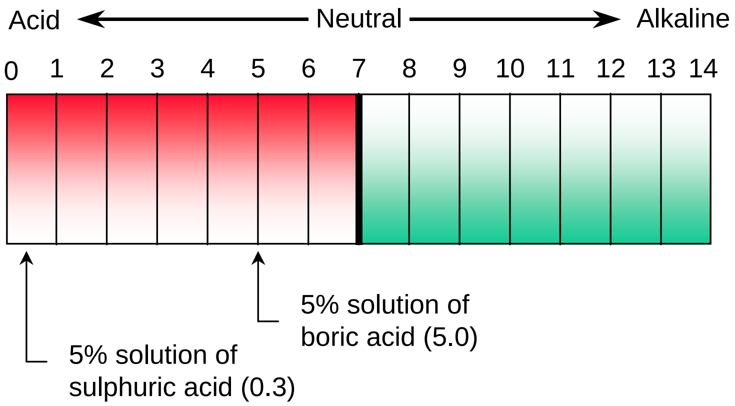

Acid
Neutral
Alkaline
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
5% solution of boric acid (5.0)
5% solution of sulphuric acid (0.3)

Figure 3.2

Comparison of the pH values of a 5% sulphuric acid solution with a 5% boric acid solution.

It might at first appear that the pH scale covers a wide range — from 0 (very acidic) to 14 (very alkaline). In reality, however, the pH scale is designed for diluted acid and alkaline solutions and is of little use in determining concentrated acidic or alkaline species.

From the above table, at pH = 0 (the most acidic on the pH scale), the hydrogen ion concentration, $[H^+]$, is 1×10^0 or 1 mole.

The term 'molarity' describes the concentration of a substance within a solution and is defined as: 'that concentration which contains that mass of substance which is equivalent to its molecular (atomic) mass in grams dissolved in one litre of water'.

Since the atomic mass of hydrogen is approximately equal to one, a 1 molar solution of acid would contain 1 g of hydrogen ions $[H^+]$ per litre or that which is equivalent to 1 part in 1000 (1000 ppm) $[H^+]$ — a relatively low concentration of acid. Table 3.2 illustrates the minimum and maximum ranges of the pH measuring scale.

Table 3.2
Minimum and maximum ranges of the pH measuring scale

pH	Hydrogen ion concentration			
	Normality (g/ℓ)	**ppm**	**ppb**	**ppt**
12	10^{-12}			
11	10^{-11}			
10	10^{-10}			0.1
9	10^{-9}			1
8	10^{-8}			10
7	10^{-7}		0.1	100
6	10^{-6}		1	
5	10^{-5}		10	
4	10^{-4}	0.1	100	
3	10^{-3}	1		
2	10^{-2}	10		
1	10^{-1}	100		
0	10^{-0}	1000		

3.4 Measurement of pH

The measurement of pH in an aqueous solution is most commonly made using a hydrogen sensitive glass electrode that forms one half-cell of an electrochemical cell. The other half-cell comprises the reference electrode that is immersed in the same solution.

The measuring circuit is completed by the meter itself — a high impedance input voltmeter used to measure the emf of the two electrodes (Figure 3.3).

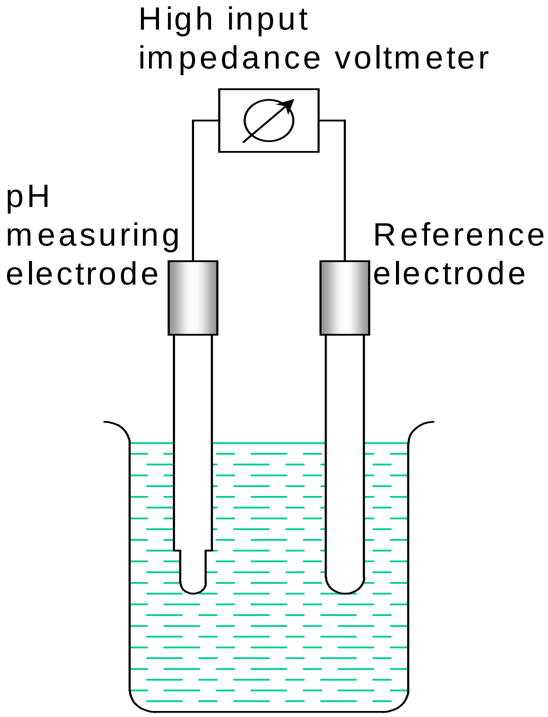


Figure 3.3
A high impedance input voltmeter is used to measure the emf of the two electrodes (Courtesy Mettler-Toledo)

3.5 The measuring electrode

The measuring electrode (Figure 3.4) comprises a glass envelope containing a buffer solution of known ionic strength and pH. A silver wire, coated with silver chloride, is immersed in the buffer solution and forms the measurement lead-off wire.

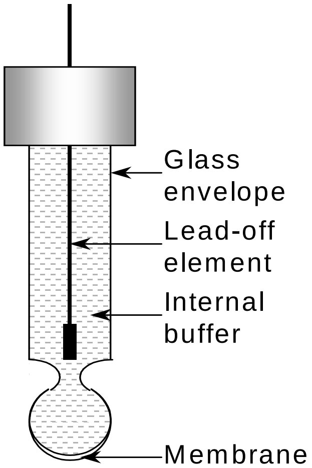


Figure 3.4
The measuring electrode comprises a glass envelope containing a buffer solution of known ionic strength and pH

The sensing element at the tip of the electrode is a hydrogen-sensitive membrane manufactured from special glass containing alkali and alkali-earth and/or rare-earth ions.

pH measurement is based on the chemical reaction that takes place between the sample solution and the membrane surface — generating an electrical potential that varies with the pH value.

The mechanism involved is dependent on hydration of the glass membrane surface which forms a gel layer (hydrated silica) when the electrode is in contact with an aqueous medium. Due to the presence of the encapsulated internal buffer, a gel layer is also formed on the internal surface of the glass membrane.

3.5.1 Hydration

A solution may be defined as a mixture in which the molecules of a substance added to a liquid are evenly dispersed. When the liquid, called the solvent, is water, the action of dissolving the substance is called hydration.

If we dissolve common salt (sodium chloride) in water, hydration occurs as a result of the charged ends of the polar water molecules attracting the ions within the ionic lattice. In this manner, the $\delta+$ charges on the water molecule attract the CL- anions and the $\delta-$ charges attract the Na+ cations. As a result the water molecules form cage-like formations around the Na+ and CL- ions — with the negative poles of the water molecules dipole pointing towards the positive Na+ cation (Figure 3.5 (a)) and the positive poles of the water molecules pointing towards the CL- anions (Figure 3.5 (b)).

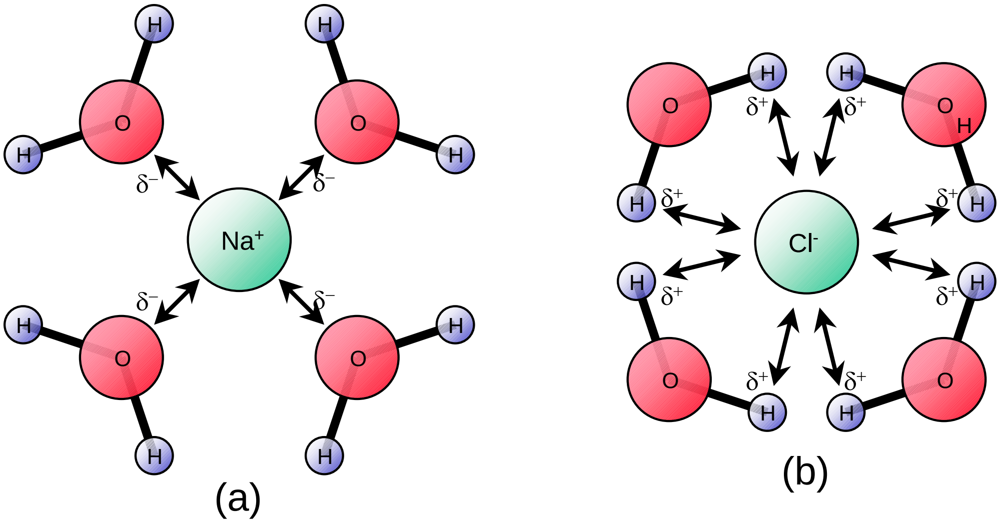

H
O
δ−
Na+
Cl-
δ+
(a)
(b)

Figure 3.5

When hydration occurs, the negative poles of the water molecules dipole point towards the positive Na+ cation (a) and the positive poles point towards the Cl^- anions (b)

The forces involved in hydration can be very strong and for many salts, if the water is evaporated, some water molecules remain attached to the ions and actually become part of the crystal. Examples include: plaster of Paris, Epsom salts, borax and washing soda.

As shown in Figure 3.6, singly charged alkali metal cations (e.g. Li^+) in the glass are exchanged for the hydrogen ions in the solution — giving rise to a phase boundary potential at the surface of the hydrated glass layer.

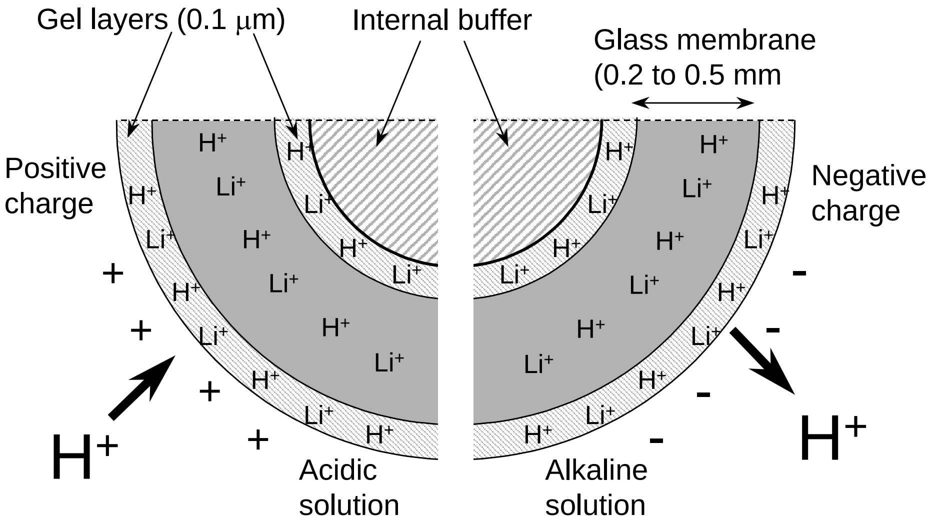

Gel layers (0.1 µm)
Internal buffer
Glass membrane
(0.2 to 0.5 mm
Positive
charge
Negative
charge
H+
Li+
+
-
Acidic
solution
Alkaline
solution

Figure 3.6

Singly charged alkali metal cations (e.g. Li^+) in the glass are exchanged for the hydrogen ions in solution (Courtesy Mettler-Toledo)

As soon as the activity of hydrogen ions is different in the two phases, diffusion of the hydrogen ion in (acid solution) or out (alkaline solution) of the gel layer occurs. This leads to a build up of charge at the outer phase layer and a new equilibrium state exists which prevents further hydrogen ion transport. The metal ions in the glass membrane are responsible for the migration of the charge to the gel layer on the inner surface of the membrane and it is this potential difference that allows pH measurement to take place.

3.6 The reference electrode

The measuring electrode forms only one half-cell of the pH electrochemical cell and in order to complete the measurement circuit it must be combined with the other half-cell — the reference electrode. In practice, the reference electrode causes more problems than the measuring electrode.

Because the reference electrode provides the reference potential, any deviation in its potential will cause the overall potential to change — thereby causing the overall pH reading to change.

The reference electrode comprises an internal reference element immersed in an electrolyte solution — both housed in a glass or plastic envelope (Figure 3.7). At the tip of the electrode a porous junction, or salt bridge, forms a liquid junction between the electrolyte and the process liquid being measured — thus completing the pH measuring circuit.

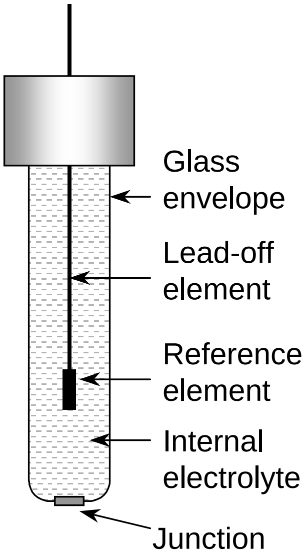


Figure 3.7
The reference electrode comprises an internal reference element immersed in an electrolyte solution and housed in a glass or plastic envelope

3.6.1 Reference element

The most commonly used reference element comprises a silver wire coated with silver chloride. When used in conjunction with a saturated potassium chloride electrolyte, it has a half-cell potential of 199 mV at 25°C.

In some electrodes the silver/silver-chloride wire is immersed direct into the internal electrolyte whilst in others the wire is surrounded by silver chloride crystals within a glass cylinder and separated from the electrolyte by a cotton-wool plug (Figure 3.8).

At one time the calomel electrode was also frequently used. The calomel electrode comprises a silver or platinum wire surrounded by a paste of mercury and mercurous chloride that is again contained within a cylinder sealed with a cotton-wool plug.

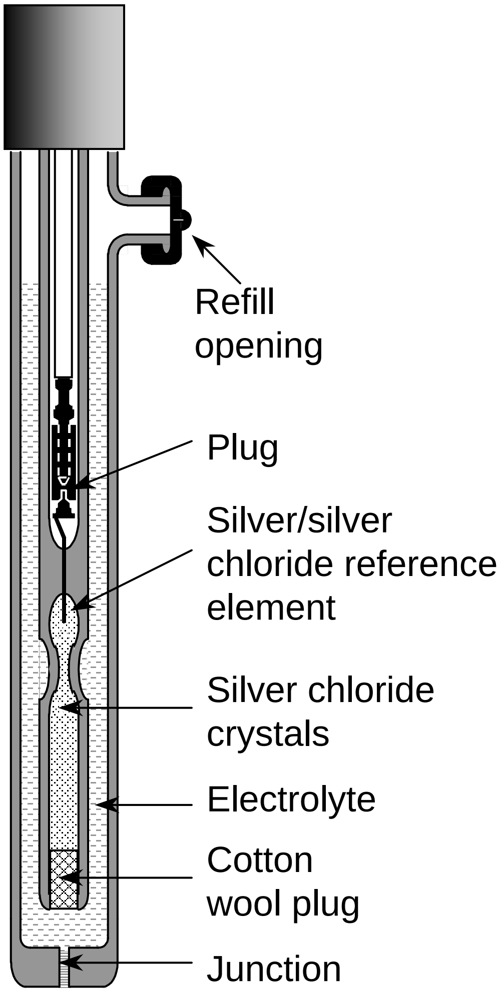

Refill
opening
Plug
Silver/silver
chloride reference
element
Silver chloride
crystals
Electrolyte
Cotton
wool plug
Junction

Figure 3.8
Construction of a reference electrode (Courtesy Mettler-Toledo)

The calomel electrode has lost much of its popularity in recent years — due mainly to its use of mercury and the potential danger of contamination to the process media and to the environment.

3.6.2 Electrolyte

In theory any conducting medium could be used as the internal electrolyte. However, the filling solution should fulfil a number of conditions:

- it should have a high ionic strength to minimise resistance
- it should be stable
- it should not react with the process solution
- it should be soluble in the process solution
- the diffusion rates of the cations and anions of the electrolyte salt should be approximately equal.

This last consideration is to prevent the build up of a charge across the liquid junction, which can cause offset errors.

The migration velocity of ions is determined by their charge and size. Table 3.5 shows the ionic mobilities of various ions at 25°C.

Table 3.5
The ionic mobilities of various ions at 25°C

Ion	Ionic mobility (cm/s.V)
Li^+	4.01×10^{-4}
F^-	5.74×10^{-4}
Na^+	5.19×10^{-4}
K^+	7.62×10^{-4}
CL^-	7.91×10^{-4}
H^+	36.25×10^{-4}

From this table it may be seen that both K^+ and CL^- ions have very similar mobilities and thus potassium chloride is the most commonly used electrolyte salt. If, for example, sodium chloride were used, where the mobilities of Na^+ and CL^- ions are quite different, a positive charge would eventually build up on the internal surface of the liquid junction since the positive Na^+ cations move slower than the negative CL^- anions (Figure 3.9).

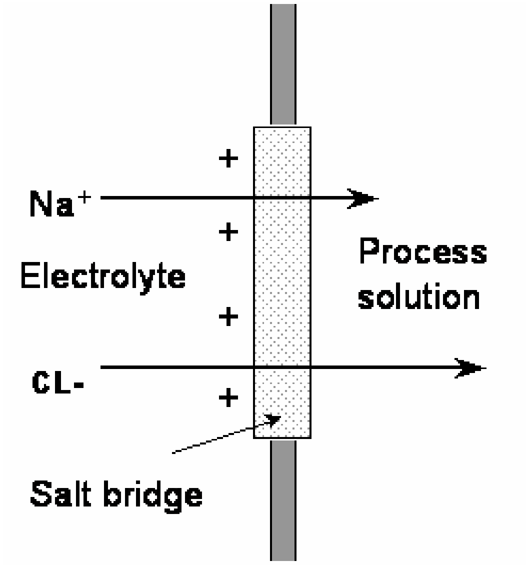


Figure 3.9
When the mobilities of Na^+ and CL^- ions are quite different, a positive charge would eventually build up on the internal surface of the liquid junction

Experience has shown that 3.0 molar KCL solutions fulfil these conditions over a wide temperature range. At higher molar concentrations, the high chloride ion concentration causes the potassium chloride to react, to some extent, with the silver chloride of the internal reference element to form soluble complexes. This can be overcome by saturating the potassium chloride electrolyte with silver chloride — thus providing a filling solution that is in equilibrium with the internal electrode. Such an electrolyte is not recommended for use with process solutions containing sulphide ions and sulphide compounds, cyanide ions and other halide ions, because of the precipitation of highly insoluble silver compounds.

Potassium chloride itself cannot be uses as an electrolyte with all process solutions since reactions can take place. Examples include: the presence of mercury (II), silver, copper (I), and lead (II) ions that react with chloride ions to form insoluble compounds.

3.6.3 Reference junction

The reference junction, also referred to as a ‘salt bridge’, liquid junction or ‘frit’, forms the interface between the process solution and the internal electrolyte and completes the electrical path from the measuring electrode to the reference electrode.

Apart from allowing small amounts of electrolyte to flow through it, the reference junction should also be chemically inert so as not to interfere with the ion exchange process. It should also maintain a low consistent electrical resistance value.

Usually, the junction comprises a ceramic frit formed in the shape of a cylindrical plug about 2-3 mm in diameter and between 3-12 mm in height. However, use is also made of a variety of porous materials including: wood, Teflon, kynar, asbestos and quartz fibres. An alternative, the ground glass sleeve junction, is mainly used for laboratory purposes and comprises two ground glass areas, mated to each other, that allow the electrolyte to permeate between them. Annular junctions, which surround the measuring electrode, are also used. Some electrodes incorporate a replaceable junction using an O-ring as the seal.

In order to prevent the process solution from flowing into the reference and contaminating the KCL solution, and/or attacking the Ag/AgCL reference element, the junction is designed to allow small amounts of the electrolyte solution to leach through it into the process.

The electrolyte housing, therefore, not only forms a reservoir for the electrolyte that is leached away, but also provides sufficient head to maintain a positive pressure. Where high process media pressures exist or high process media temperatures could produce reversed flow across the liquid junction, this pressure could be insufficient. Consequently, the filling hole is often connected to a further electrolyte reservoir or pressure source (Figure 3.10).

Many of these problems are overcome in modern electrodes that make use of a gelling agent that is added to the electrolyte solution. Apart from slowing down the effects of contamination through the porous junction the gel-fill may be sealed with a positive pressure since it is less susceptible to being forced out of the junction during periods of heat or pressure cycling.

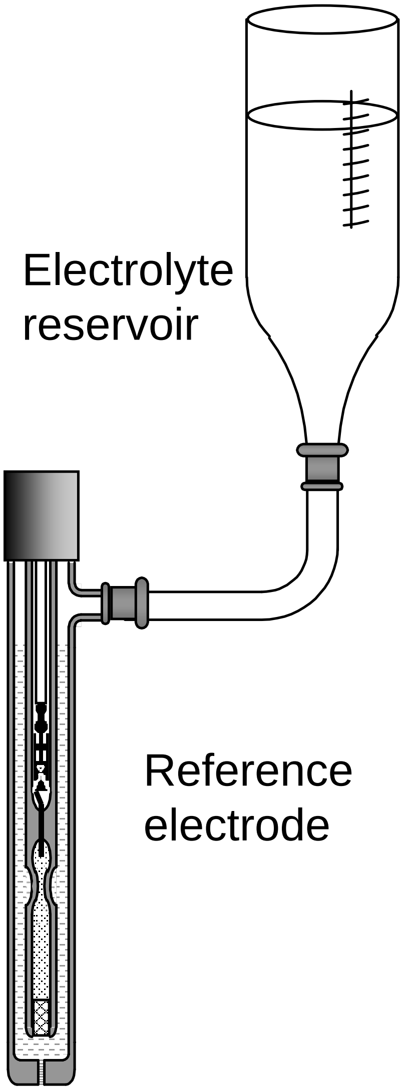


Figure 3.10
Increasing the positive pressure across the liquid junction through the use of a further electrolyte reservoir or pressure source

3.6.4 Reference construction

In practice, the measuring and reference electrodes are usually combined into a single unit (Figure 3.11) in which the reference electrode is arranged concentrically around the measuring electrode.

The combination electrode is much easier to handle than separate electrodes and is, therefore, used almost exclusively in industrial applications. Only when the two electrodes are expected to have very different life expectancies is the use of separate electrodes recommended.

Apart from preventing contamination of the internal environment of the reference electrode, it is also important to prevent coating forming over the junction.

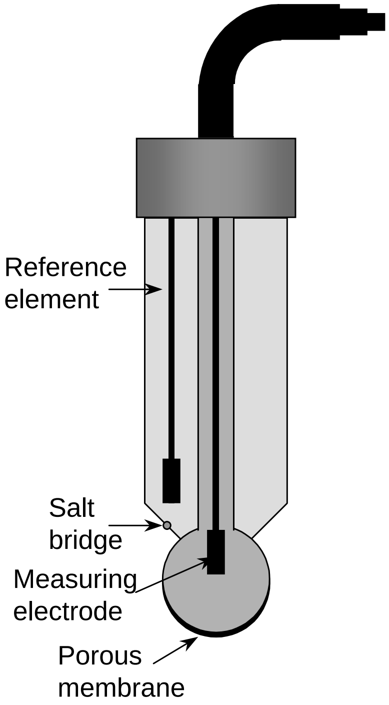


Figure 3.11

Combination electrode in which the reference electrode is arranged concentrically around the measuring electrode

The liquid junction can be blocked if the stream contains any material that reacts with the filling solution to form a precipitate. Particularly troublesome are silver, lead and mercury, which form insoluble chlorides.

This may be overcome using the double-junction reference electrode which is essentially a complete electrode with its own liquid junction fitted within an electrode outer body having a second liquid junction in contact with the sample. The main advantage of this electrode is that the reference solution in the outer body , usually potassium chloride, can be chosen to be compatible with the 'inner' electrode solution and the sample. Clogging of the outer junction is extremely unlikely, since neither potassium ions nor chloride ions form insoluble compounds with the majority of materials found in process streams. Blocking of the inner junction is not possible.

3.7 Nernst equation

The Nernst equation relates the cell potential with the hydrogen ion concentration:

$$E = E^o + 2.303\frac{RT}{nF}\log\left[H^+\right]$$

where:
E = potential generated (in millivolts)
E^o = standard cell potential
R = universal gas constant
T = absolute temperature (K)
n = valency (charge) of the ion (n = 1 for H^+ ion)
F = Faraday's constant
$[H^+]$ = hydrogen ion concentration

The term $2.303\frac{RT}{nF}$ is called the 'Nernst' or 'Slope' factor and is given the symbol N and the equation becomes:

$$E = E^o + N \log[H^+]$$

Thus at 25°C if the pH changes from 7 to 8 the voltage output will change from 0 to 59.16 mV. Similarly a change in pH from 8 to 9 will result in a voltage change from 59.16 to 118. 32 mV.

Table 3.6 shows the expected mV output for a number of pH values at 25°C, whilst Figure 3.12 illustrates this.

Table 3.6
mV output for a number of pH values at 25°C

pH	ΔpH	E = -N (Δ pH)
0	+7	414.11 mV
1	+6	354.95 mV
2	+5	295.79 mV
3	+4	236.64 mV
4	+3	177.48 mV
5	+2	118.32 mV
6	+1	59.16 mV
7	0	0 mV
8	-1	- 59.16 mV
9	-2	-118.32 mV
10	-3	-177.48 mV
11	-4	-236.64 mV
12	-5	-295.79 mV
13	-6	-354.95 mV
14	-7	-414.11 mV

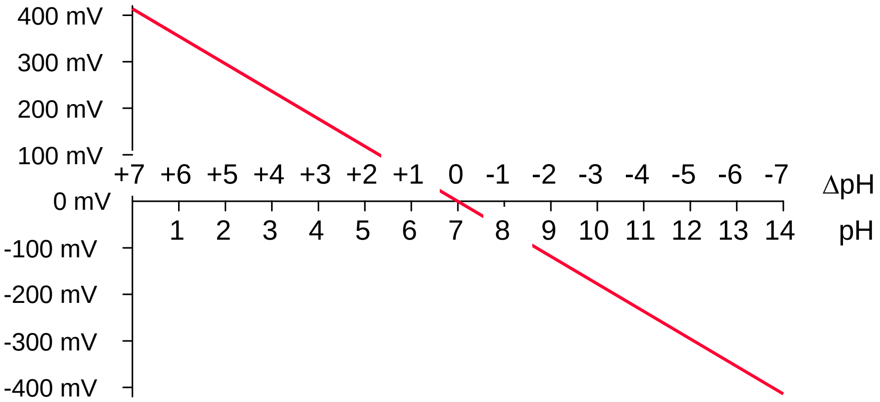


Figure 3.12
mV output for a number of pH values at 25°C

3.7.1 Temperature effect

It should also be very apparent that the 'Nernst factor' also determines the number of millivolts for each pH unit at different temperatures. This is shown in Table 3.7.

Table 3.7
Expected millivolt output for each pH unit at different temperatures

Temperature (°C)	mV/pH decade
5	55.19
10	56.18
15	57.17
20	58.17
25	59.16
30	60.15
35	61.14
40	62.14
45	63.13
50	66.12
55	65.11
60	66.10
65	67.10
70	68.09
75	69.08

In effect, the effect of temperature is to change the slope of the response as shown in Figure 3.13. Since the change in output vs. temperature is linear, it can be expressed as 0.00335 pH error/pH unit/°C.

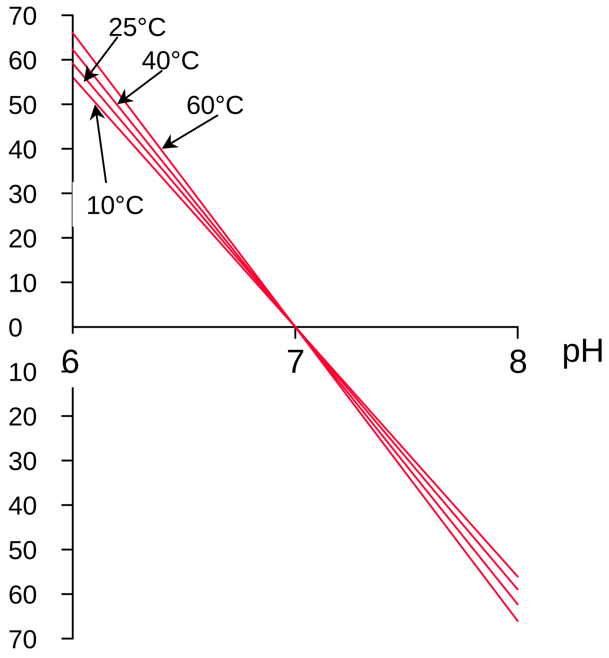


Figure 3.13
The effect of temperature changes the slope of the response

Thus, if an uncompensated pH system were standardised in a pH 7 buffer at 25°C, then a sample that measured pH 3 at 15°C, would have an error of:
0.00335 x 10°C x 4 units = 0.134 pH unit

And at 75°C (probably close to a typical worst case), a 3 pH sample would read 3.67 pH using an uncompensated pH system.

Clearly, then, the measurement of pH must also involve the measurement of temperature in order to compensate for the errors due to the Nernst slope.

3.8 Antimony electrode

When measuring effluents containing hydrofluoric acid (HF), which attacks glass, use is often made of the antimony electrode. Used with a conventional reference electrode, the antimony electrode consists of a plastic body with an antimony ring fitted into the end (Figure 3.14).

When first immersed in a solution containing oxygen, the surface of the antimony oxidises to form the pH responsive layer. The electrode also usually includes a built-in scraper or grinding mechanism that is used to restore the electrodes performance should it become coated during use.

Because the antimony electrode is extremely rugged, it is often used for determining the pH of soils. Further, because antimony is extremely hard, it may be used in high flowing abrasive liquids (slurries) that would normally grind electrodes away.

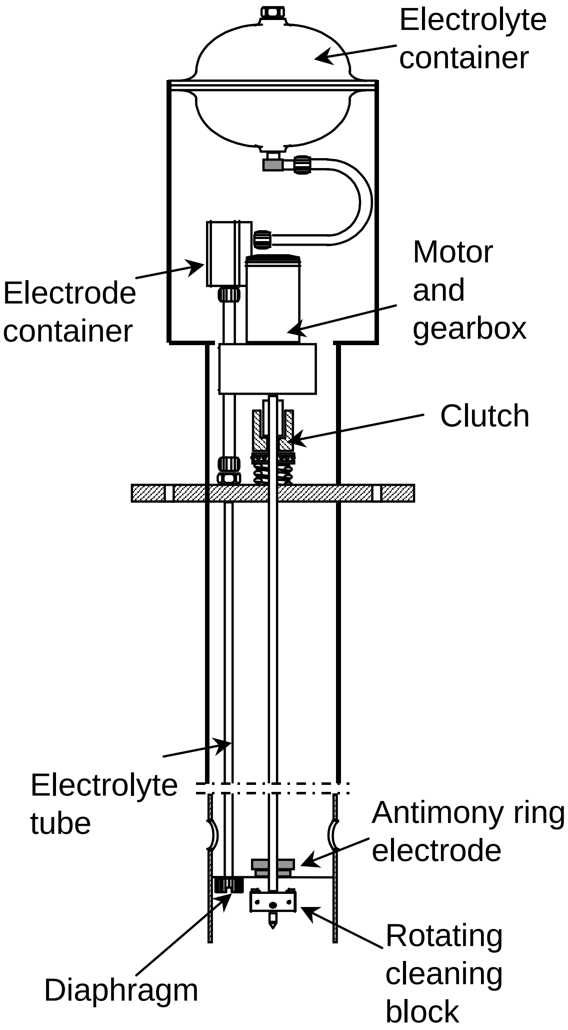

Electrolyte container
Electrode container
Motor and gearbox
Clutch
Electrolyte tube
Antimony ring electrode
Rotating cleaning block
Diaphragm

Figure 3.14
Basic construction of an antimony ring electrode

However, antimony ring electrodes have many disadvantages:

- since it is a metal electrode it will respond to Redox potentials;

- any metal more noble than antimony i.e. having a standard half-cell potential greater than antimony, will deposit on the electrode;
- at pH = 7 the potential of the antimony measuring chain is approximately -400 mV and compensation within the circuitry of the transmitter must be made to accommodate this potential shift;
- the slope of the antimony measuring chain differs to that of the glass electrode 52 to 57 mV/decade;
- the response is close to Nernstian only over a narrow range and thus temperature compensation is only effective over the pH range 2 to 7;
- antimony and antimony oxide are poisonous.
- the best reproducibility normally attained is about 0.1 pH
- response time is poor (from 3 to 30 minutes)

Because there is so much more uncertainty to every aspect of behavior of the antimony electrode compared with the glass electrode, it should be considered only as a last resort.

Even when working with hydrofluoric acid it should be noted that HF solutions above 4 pH do not have such detrimental effect on glass electrodes. Under these circumstances it may be better to use a glass electrode offering superior performance despite a relatively short life.

3.9 Sources of errors

The measurement of pH is subject to a wide number of potential errors and in order to ensure accuracy of measurement, each must be taken into account.

3.9.1 Solution temperature coefficient

While temperature compensation is applied for changes in the electrode pair output, both in terms of slope and zero offset, it should be remembered that most solutions change their pH value with temperature variation (Figure 3.15).

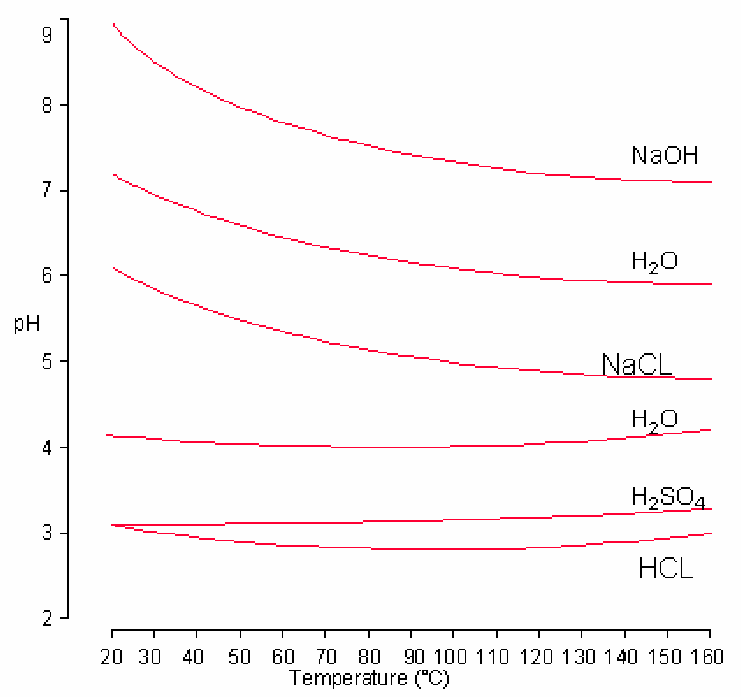


Figure 3.15
Effect of temperature on the pH of various solutions

For some applications, it is possible to refer the value to a reference temperature, e.g. 25°C, so removing the effect on the measurement of temperature change. Compensation has also been incorporated into the design of several industrial pH meters.

3.9.2 Activity vs concentration

Although pH is based on the [H^+] concentration, we in fact measure the hydrogen activity. And whilst we assumed that the activity of the hydrogen ion (aH^+) is directly proportional to the [H^+] concentration, this is not always the case.

The most important variable affecting the activity is the ionic strength of the solution in which the presence of ions of certain compounds tends to limit the mobility of the hydrogen ion — thereby decreasing the activity of H^+.

For dilute solutions where the ionic strength is low the activity of hydrogen ion is equal to its concentration. However, as the ionic strength of a solution increases, the activity coefficient decreases — lowering the mobility of the hydrogen ion and increasing the pH.

Normally, a hydrogen ion concentration of 0.001 mol/ℓ renders a pH of 3 and a molality of 0.01 mol/ℓ renders a pH of 2. However, in the vast majority of pH measurements the process media contains the ions of other compounds and produces what is termed the 'salt effect'. Examples of compounds producing the salt effect include: sodium (Na^+) sulphate ($S0_4^{2-}$), calcium (Ca^{2+}) chloride (CL^-), and potassium (K^+) nitrate (NO_3^-). The presence of these ions in a solution tends to limit the mobility of the hydrogen ion, thereby decreasing the activity of H^+. Thus, for example, the presence of 0.1 mol/ℓ potassium chloride in a 0.001 mol/ℓ solution of hydrochloric acid would give rise to a pH reading of pH = 3.081 (an error of 2.7%).

And for 0.09 mol/ℓ potassium chloride in a 0.001 mol/ℓ solution of hydrochloric acid (total molality = 0.1 mol/ℓ) the pH would measure pH = 2.081 (an error of 4%).

Another source of error related to the activity is the 'medium effect' — what effect the type of medium solvent will have on the hydrogen ion activity. Whilst this effect may be ignored where measurements are made in aqueous solutions, the H^+ activity in ethanol, for example, is 200 times greater than in water.

Because pH measuring chains are usually calibrated using aqueous standard buffers, it is therefore impossible to find a correlation between the H^+ activity in an aqueous solution and in a non-aqueous solution.

3.9.3 Asymmetry potentials

In our discussions on the Nernst equation, it was seen that the mV output of the pH electrode at pH = 7 was 0 mV. In other words, when the electrode is immersed in a solution having same pH as its internal buffer solution (pH = 7), the potential across the glass membrane should be zero.

In practice, even with a new, properly stored electrode, an offset potential, usually a few millivolts or less, exists. Anything which modifies the ion exchange mechanism — a dehydrated electrode, using the electrode in a non-aqueous solution, plugging or coating of the glass surface, etc. —.will change this potential.

Another offset potential is to be found when the measuring and reference electrodes are immersed in a zero pH solution. This potential constantly changes depending on the pH value, temperature, time, age of the electrode and the type of glass formulation used.

Together, these offsets are referred to as ***asymmetry potentials*** and are usually compensated for during calibration of the sensor assembly.

Routine cleaning of the electrode and junction prior to calibration should minimise the effect of the asymmetry potentials. However, once the asymmetry potential has increased beyond the instruments calibration correction capability, changing the electrolyte solution and the junction may still prove effective.

3.9.4 Alkaline error

Alkaline error (also referred to as sodium ion error) is the result of sodium ions, partly or completely, replacing the hydrogen ions — thus decreasing the hydrogen ion activity and artificially suppressing the true pH value.

Sodium ion interference occurs when the hydrogen ion concentration is very low and the sodium ion concentration is very high. The effect thus increases with increasing pH value (pH > 9) as well as increasing temperature (Figure 3.16).

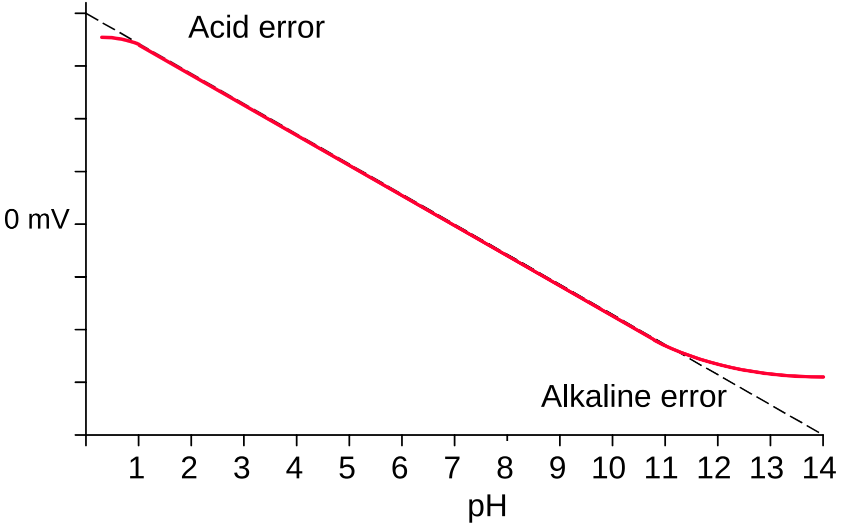


Figure 3.16
Sodium ion interference increases with increasing pH value (pH > 9) whilst acid error is rarely seen above acid levels of 1 pH (Courtesy Mettler-Toledo)

Since there is no glass formulation currently available with zero sodium ion error, it is important that the error be consistent and repeatable. Such characteristics are available when controlled molecular etching is applied to the glass membrane. This provides a consistent amount of lithium ions that are available for exchange with the hydrogen ions to produce a similar milli-volt potential for a similar condition.

3.9.5 Acid Error

As pH decreases, acid molecules are absorbed by the gel layer — leading to a decrease in the H+ activity and a thinning of the gel layer due to acid stripping.

This influences the mV output by causing an artificially high pH value to be registered.

The acid error changes very little with temperature and, again as shown in Figure 3.16, is rarely seen above acid levels of 1 pH.

3.9.6 Glass electrode impedance

Whilst glass is usually considered to be a near perfect insulator, in reality the glass electrode is an ionic conductor whose resistance changes according to the solution temperature — decreasing as the temperature rises.

Because the pH responsive membrane is in series with the electrical circuit it should have as low a resistance as possible whilst combining good pH response, durability and mechanical strength. These requirements cannot be achieved with a single type of glass membrane for all applications. As a result, three different types of glass electrode are produced (Figure 3.17).

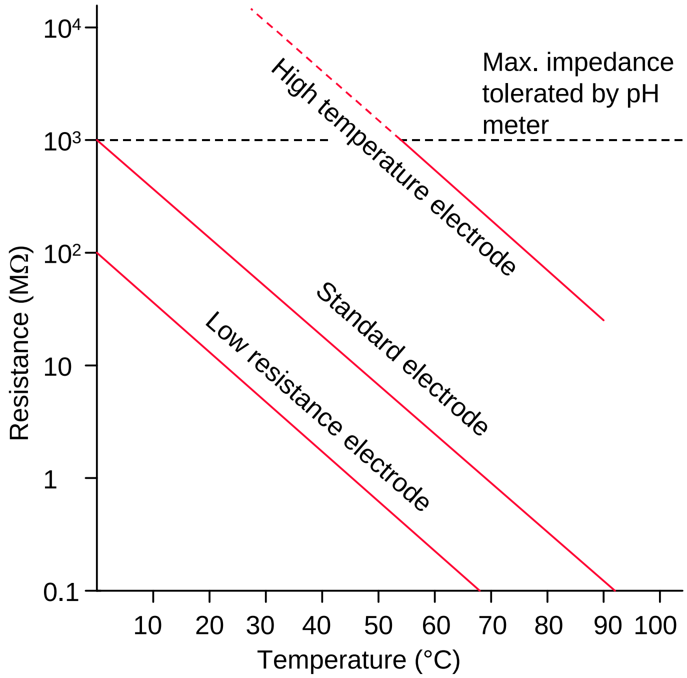


Figure 3.17
Three different types of glass electrode: 'standard'; 'low resistance'; and 'high temperature' (Courtesy ABB Kent)

The 'standard' membrane glass, used for the majority of purposes; has a good response over 0 to 14 pH and can be used between 0 and 100°C. The 'low resistance' membrane glass has a much faster pH response by a factor of 10 (because of its lower resistance) but can only be used over a pH range of 0 to 10 and up to temperatures of 60°C. And the 'high temperature' membrane glass is used at temperatures between 50 and 130°C.

Consequently, the resistance of the membrane glass can lie between 1 and 1000 MΩ depending on the process temperature and the type of electrode selected. In order to develop most of the electrode potential across the input impedance of the pH meter, and to minimise the effect of impedance variations due to changes in temperature, the pH meter input impedance needs to be at least 1000 times higher than the maximum electrode impedance of 1000 MΩ, i.e. 10^{12} Ω (Figure 3.18).

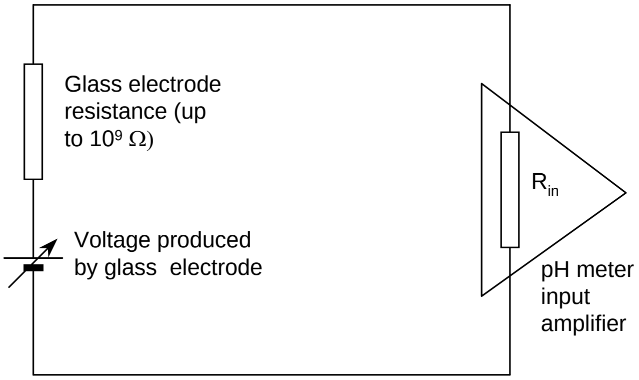

Glass electrode resistance (up to 10⁹ Ω)
Voltage produced by glass electrode
R_in
pH meter input amplifier

Figure 3.18
Input impedance of pH meter needs to be at least 1000 times higher than the maximum electrode resistance to ensure most of the electrode potential is developed across it

Fortunately, modern high input impedance amplifiers are now available in the range 10^{13}-10^{14} Ω. Thus, with an amplifier having an input impedance of 10^{13} Ω, for example, the error due to impedance matching is less than 0.01% and a change in electrode impedance from 1 to 1000 MΩ will effect the voltage by only 0.001%.

The main implications of the very large electrode source impedance lies in maintaining the high insulation in all electrode terminations. This insulation has to be maintained, not only between the glass and reference terminations, but also between glass and earth, since the solution is often at earth potential.

The most common problem encountered, especially in damp conditions, is low insulation of the electrode terminations. In addition, replacement components must be carefully chosen in order to obtain a high measurement integrity, since construction materials used in many plugs and sockets and termination blocks are totally inadequate for pH use due to their low insulation.

Although the insulation of the electrode terminations cannot be measured directly, due to the lack of commercially available insulation testers, the presence of low insulation can be determined using a pH electrode simulator. This device, a vital piece of test equipment for any fault finding investigations on pH systems, is basically a mV source with the added feature of being able to switch in a 1000 MΩ resistor into the glass electrode output lead to simulate the impedance of the electrode.

Calibration

In the pH vs mV curve of Figure 3.19, we can see that there are two deviations that may occur from the ideal relationship at a given temperature: zero shift and slope deviation.

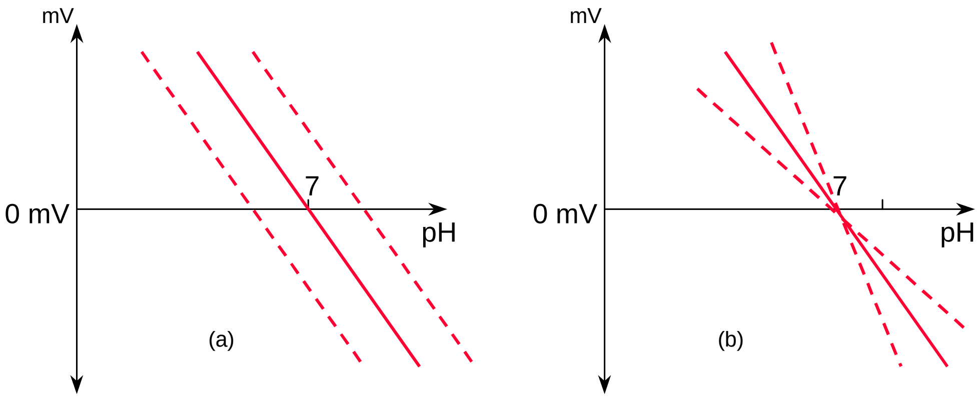


Figure 3.19
(a) Zero shift moves the curve along the x axis (b) slope deviation alters the slope from 59.16 mV/decade

Zero shift occurs when the reference electrode no longer performs correctly or if the pH electrode itself is fouled. The effect is to move the curve along the x axis i.e. the potential is no longer 0 mV at pH = 7 but at, for example, pH =6 or 8. Most analysers allow an adjustment of ± 2 pH units.

The effect of slope deviation is to alter the slope from 59.16 mV/decade. Because it is not possible to always manufacture electrodes with a 100% response a slope adjustment of 95 to 105% is usually allowed in most instruments. Other factors affecting the slope are due to faulty manufacture, ageing of the electrode or fouling of the membrane.

Since both these errors must be catered for, two-point calibration is usually performed using a buffer solution. A buffer solution is a pH solution that maintains a nearly constant pH if diluted or concentrated and despite the addition (possibly due to contamination) of small amounts of acid or alkali. Standard buffer solutions are available from instrument suppliers and normally span the following ranges:

'pH 1'	DIN 19267	0.1 M hydrochloric acid.
'p H4'	BS1647	0.05 M potassium hydrogen phthalate.
'pH 7'	Mixture of disodium hydrogen phosphate and monopotassium dihydrogen phosphate.	
'pH 9'	BS 1647	0.05 M disodium tetraborate (borax).
'pH 10'	BS1647	0.025 M sodium hydrogen carbonate + 0.025 M sodium carbonate.

Normally the zero shift is set first using a buffer with pH = 7 (Figure 3.20(a)). Next, the slope is set using a buffer with a 2 to 3 pH unit difference from the first (Figure 3.20(b)). Since the electrode response may not be perfectly linear across the entire 0-14 pH range, a pH buffer with a value greater than 7 (e.g. pH = 9 or 10) is used when measurements above 7 are carried out and vice versa.

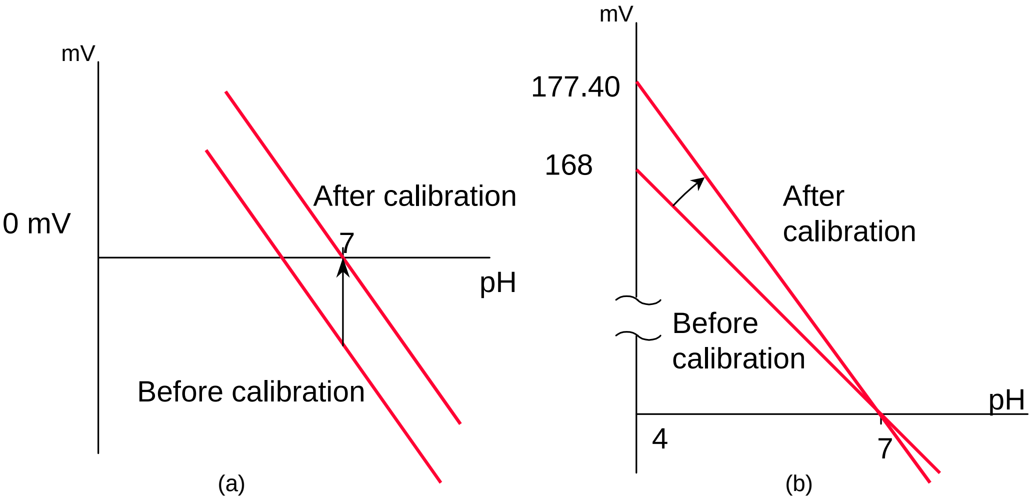


Figure 3.20

(a) The zero shift is set first using a buffer with pH = 7. The slope is set using a buffer with a 2 to 3 pH unit difference from the first e.g. pH = 4

In some cases, ‘bracketing’ of the measured value may be necessary in which two buffers, one below and one above the average measured value, are used. This ensures greater accuracy over the measurement interval.

3.10 Applications

3.10.1 High-purity water and pH

(Courtesy: MILLIPORE APPLICATIONS Technical Library)

pH influences the rate of many chemical and enzymatic reactions. Therefore, buffered solutions are commonly utilized in the laboratory. These solutions are usually prepared with high-purity water in order to minimize the risk of contamination with water impurities. Discussed here are the difficulties and alternatives to measuring the pH of high-purity water and the impact of buffer dilution on pH.

pH of high-purity water

The pH of water is defined as the negative logarithm of the hydrogen ion activity, which is often assimilated to the hydrogen ion concentration (Equation [1], Table 3.8). While the pH of pure water is approximated to be 7.0 at 25°C, the theoretical value is 6.998. Indeed, the dissociation of water and the ionic product for water (Equations. [2] And [3], Table 3.8) indicate that $10^{-6.998}$ mol/L of H_3O^+ are present in pure water. However, one cannot measure the pH of high-purity water simply by dipping the electrodes of a pH meter into a beaker full of water. This measurement is challenging due to the quasi-absence of ions that would enable electron transport between the measuring and reference sides of the pH electrode. It often results in erratic and meaningless pH readings.

Adding the slightest amount of acid or base to pure water will change its pH significantly. Pure water readily absorbs carbon dioxide (CO_2) when exposed to the atmosphere, which forms carbonic acid (Eq. [4], Table 3.8). Carbonic acid dissociates into bicarbonate that is in equilibrium with carbonate. Dissolution of CO_2 in water ultimately leads to a pH of approximately 5.8.

Table 3.8

A quick reference guide of basic definitions and equations

Definitions	**Equations**
(1) Definition of pH	$pH = -\log [H_3O^+]$
(2) Dissociation of water	$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
(3) Ionic product for water	$K_w = [H_3O^+]\cdot[OH^-]$
(4) Carbon dioxide in water	$CO_2 + H_2O \rightleftharpoons H_2CO_3$ $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ (pKa = 6.35) $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ (pKa = 10.33)
(5) Conductivity of water	$\chi = F.\sum C_i z_i u_i$
(6) Henderson-Hasselbalch	$pH = pK_a + \log \frac{[A^-]}{[HA]}$

It is this pH value that is eventually obtained if one measures the pH of ultrapure water without working under controlled conditions.

The issues linked to the pH measurement of ultrapure water are addressed in various references. The United States Pharmacopeia (USP) recommends the addition of potassium chloride (KCl) to alleviate the problem. A more precise and complex experimental setup and method for the pH measurement of pure water are described in an American Society for Testing and Materials (ASTM) Standard Test Method. It includes the use of a flowthrough sample chamber and the addition of KCl via a reference electrode with positive electrolyte leakage. Other standards, such as the International Organization for Standardization (ISO) 3696 standard, simply do not require the pH measurement of pure or ultrapure water. They rely on other physicochemical parameters to characterize water quality, such as conductivity.

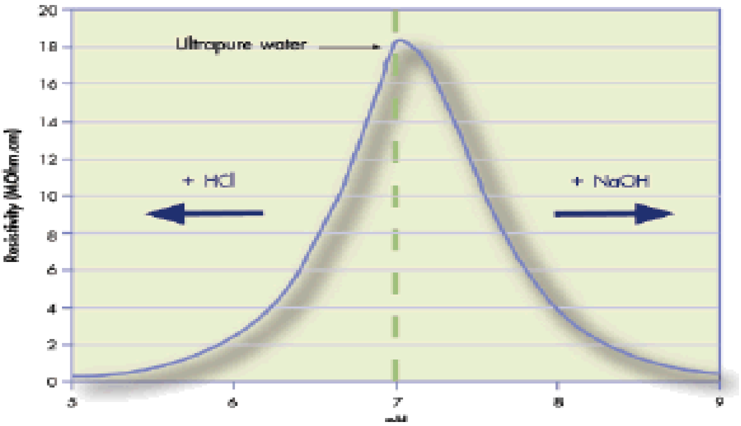


Figure 3.21

Theoretical resistivity values of water following the addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH). The resistivity of ultrapure water is 18.18 MW.cm and the pH is 6.998

Conductivity of high-purity water

A conductivity measurement may be used as an alternative to the pH measurement of high-purity water. Conductivity measures the flow of electrons through a fluid, which is proportional to the concentration of ions, their charge, and mobility (Equation. [5], Table 3.8). The relationship between resistivity (the reciprocal of conductivity) and the pH of water is illustrated in Figure 3.21. When only pure water is present, a conductivity value of 0.055 S.cm–1 at 25°C is measured. This results from the water dissociation into hydroxide and hydroxonium ions. Therefore, at 25°C, a conductivity of 0.055 $S.cm^{-1}$, or a resistivity of 18.18 MΩ.cm, implies that the water is ultrapure and that the pH is inherently 6.998.

Diluting buffer solutions

The pH of a buffer solution composed of a weak acid and its conjugate base is related to the dissociation constant (pK_a) of the acid/base pair, as shown in Equation.[6], Table 3.8. By definition, buffers are resistant to large changes in pH. However, in the laboratory setting it becomes evident that diluting a buffer with pure water impacts the pH of the solution. Several parameters might explain these pH variations.

1. Temperature. Activity coefficients and equilibrium constants vary with temperature, which causes the pK_a and pH of a buffer to change. Temperature coefficients vary significantly with the nature of the buffer (–0.028 pH/°C for Tris and –0.0028 pH/°C for phosphate). For this reason, temperature is usually reported along with pH values. The pH of water itself varies with temperature: 7.27 at 10 °C, 7.00 at 25 °C, and 6.63 at 50 °C.
2. Buffer capacity. Buffer capacity is the ability of a buffer to resist changes in pH. It depends on the total concentration of the acid/base pair and the concentration ratio. Buffer capacity is high when solutions are concentrated, the ratio of acid to base is close to 1, and the pH is ±1 unit from the pK_a.
3. Ionic strength. Ionic strength describes the amount of electric charges in a solution. It is a function of the concentration and the valence of the ions present. High ionic concentration tends to limit the mobility of the hydrogen ion, which decreases its activity and influences the pH measurement.
4. Dilution. Related to a decrease in ionic strength, dilution directly impacts the pH of a solution. For example, the dilution of a 0.1 M buffer system (HA/HA^-) with an equal volume of water results in a pH change of 0.024 units. The pH variation of $HA^-/A2^-$ buffer systems, such as phosphate, is three times that value.

Conclusion

High-purity water is often used in the laboratory to avoid possible artifacts caused by water impurities. Measuring the pH of this water is challenging and necessitates specialized equipment. However, using water with high resistivity (18.2 MΩ.cm at 25 °C) ensures that the pH is close to 7.0. Diluting buffer stock solutions with high-purity water leads to pH changes. These variations in pH are unavoidable and can be explained by changes in ionic strength and buffer capacity.

3.10.2 pH and redox sensors

Some of the sensors from the industry and their features are discussed here.
(From METTLER TOLEDO)

Ph & Redox Sensor from mettler Toledo

Monitoring of the parameters pH and redox (ORP) is most important in many different industry processes to reduce cost and optimize the yield. The requirements of many industry processes are different. In chemical processes the material has to withstand acids or caustic strong solutions under for example high temperatures. The electrodes must also be certified for use in hazardous areas.

In pharmaceutical and food processes measuring systems have to meet hygienic design, and must withstand many sterility cycles and provide traceability for validation purposes. pH measurement in high purity water requires special precautions. The high purity pH assembly uses a shielded flow chamber and a permanent outflow of reference electrode for stable measurement and a 3-way valve for in-line calibration.

3.10.3 SevenMulti™ Version 2.0

S40-K SevenMulti pH meter from Mettler Toledo

This model of the pH measurement unit from Mettler Toledo supports the following features.

- Increased sample throughput through automated dual-channel GLP measurement and calibrations using the Rondolino sample changer. A barcode reader can be connected to read in the sample ID.
- PIN number based access control avoids accidental changes to the measurement settings.
- The LabX software provides direct connectivity with Microsoft Excel for data transfer.

3.10.4 InPro4501VP

XEROLYT®PLUS polymer electrode from Mettler Toledo

InPro4501VP is a rugged pH-electrode with PVDF shaft, built-in temperature sensor and Solution Ground with diagnostics for chemical applications and high flow-through rates. Also available with fixed cable.

Features and benefits

Low maintenance: A solid XEROLYT®PLUS polymer electrolyte (no refilling and pressurizing) in direct contact with the process media via an open junction. No clogging in contaminated media due to the open junction.

Reliable measurements in heavily contaminated liquid media: It is suitable in industrial processes or in wastewater applications with highly contaminated solutions, emulsions and suspensions, sulfide-bearing media, suitable also for high flow-through rates. The solution ground assures accurate measurements with a built-in sensor diagnostics tool.

Rugged PVDF body design: Dual 1" NPT threads allow the sensor to be screwed directly into immersion tubes, pipes, process vessels, etc., due to the polymer body design, protecting the electrode from mechanical damage, acting as a housing at the same time.

Flat membrane for abrasive media: The electrode has a flat glass membrane with protective stand-offs, for media with high content of fibers, particles, etc.

Specifications

Short description	low-maintenance pH-electrode with PVDF body
pH-range	1...14
Temperature range	0...100 °C (32...212 °F)
Pressure resistance (bar)	0...7 bar up to 65 °C, 3.5 bar at 100 °C
Pressure resistance (psi)	0...100 psi up to 150 °F; 50 psi at 212 °F
Diaphragm	open annular junction
Reference system	Argenthal system
Solution Ground	yes, with diagnostics
Sterilizable	no
Autoclavable	no
Shaft material	Polymer PVDF, diameter: 28.5 mm or 1.12"
Connector	VarioPin (VP) IP68 resp. fixed cable
ISM	no

3.11 Troubleshooting

3.11.1 Linearity error

- There is some deviation from a linear pH response even in the range where neither alkaline no acidic error is exhibited.
- Error may be different for every pH glass composition.
- The simple compositions show most linearity.
- Maximum for such an error may be about 0.04 pH but could compound with other potential errors Depends to a lesser degree on the buffer solutions used

3.11.2 Temperature range

- Most pH electrodes will work within -5 to 105 °C
- The general limiting factor is the reference electrode
- Short term usage may exceed specified continuous temperature limit by 20 °C
- For use in non aqueous solutions and under pressurized conditions limit may go up to 150 °C

3.11.3 Limitations

Solubility of pH glasses

- pH glasses in reality are only mixtures of oxides, transparent but otherwise do not exhibit all characteristic of real glasses.
- Many are soluble in low conductivity solutions especially in distilled, deionized and ultra pure water.

- Continuous drift, frequent calibration and short service life will result from pH glass dissolution. The dissolving process will accelerate at elevated temperature
- There are no data available for selecting the right electrode, trial and error will provide the answer

The solution temperature effect

- When temperature changes, the actual pH of the solution being measured can change. This change is not an error caused by the change in temperature. It is the true pH of the solution at the new temperature. Since this is not an error, there is no need to correct or compensate for this temperature effect.

The pH electrode temperature effect

- There is only one major temperature effect in pH measurement that can cause errors in readings. This is the change in the electrode's response (or sensitivity) to pH that results from change in temperature. It is the only reasonably predictable error due to changes in temperature, and is the only temperature related factor that pH instruments with temperature compensation can correct

3.11.4 pH measurement of photographic processing solutions - sources of errors

1. Covering or capping sample solutions and buffers during temperature equilibration to 25°C reduces aerial oxidation and prevents dilution, evaporation, or contamination of solutions.
2. Using either NIST or calibrating buffers that are contaminated or expired may prevent meter calibration within the specified buffer tolerances.
3. A change in temperature of 1°C produces a change of 0.015 - 0.020 pH unit in carbonate-buffered developers of pH 10. For photo processing solutions of higher pH that are not as well buffered, this variation with temperature can be 0.03pH unit per °C or greater. Because of this effect, careful control of temperature is essential to precise and accurate measurement of pH.
4. Stirring is required during both meter calibration and sample pH measurement for the best precision, in measurements on the NIST phthalate buffer (pH 4), 95 percent confidence limits for a single analyst were ± 0.023pH without stirring the buffers and test sample, and ± 0.007pH with stirring (based on ten measurements by each method, recalibrating the meter between measurements).
5. Clogging of reference electrode junctions occurs quite readily in photo processing solutions due to the high ionic strengths and complicated matrices. Reference electrodes can be tested in several ways for proper performance. Reference electrodes with ceramic frit or plug-type junctions gave good response when new, but should be checked regularly for electrolyte flow, based on the frequency of measurements made. Sleeve-type junction reference electrodes gave the best accuracy and precision. However, due to the high flow rate of filling solution, close attention is required from the analyst to ensure that the electrode has adequate filling solution and that the electrolyte is not allowed to drain completely into the sample to be measured. This is necessary both for proper performance of the electrode and to avoid sample contamination.
6. In meter calibration, slope may be determined by adjusting a manual slope control or reading a slope value calculated by the meter. Historically, 95 percent of Nernstian electrode response has been used as the cut-off point for continued use of electrodes for pH measurements. The industry now uses slope criterion for electrode use based on a 4 percent window that starts at the maximum new electrode slope (for the model of pH electrode being used) to determine if an electrode can be used to measure the pH of a sample. Therefore, for a pH electrode which typically has a slope of 102 percent when new, such as CORNING 476024, the appropriate slope range would be 98-102 percent. Outside of this range, the analyst may be unable to calibrate the meter within the buffer tolerances specified in the method.

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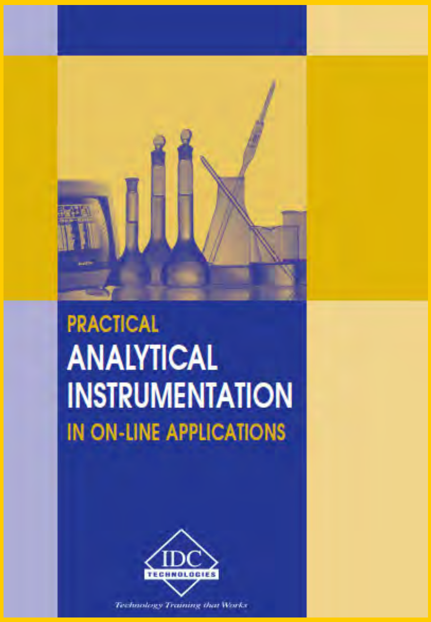
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