

Theoretical Analytical Chemistry

First stage

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By

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2019-2020

Introductions

Chemistry is the study of matter, including its composition, structure, physical properties, and reactivity. There are many benefits to studying chemistry, so we can divide it into five fields: organic, inorganic, physical, biochemical, and analytical.

Analytical Chemistry

It is the field that studies the structure of compound and determination the element present in the structure.

Classical methods use separations such as precipitation, extraction, and distillation and qualitative analysis by color, odor, or melting point. Quantitative analysis is achieved by measurement of weight or volume.

Analytical chemistry is also focused on improvements in experimental design, chemometrics, and the creation of new measurement tools to provide better chemical information.

Analytical method is classification to:

- Qualitative analysis
- Quantitative analysis
- Instrumental analysis

Qualitative analysis:-

It is the operation used to know the type of species present in compound or mixture.

Quantitative analysis:-

It is the operation used for determination the quantity of species present in substances or mixture in unit.

Quantitative analysis refers to analyses in which the amount or concentration of an analyte may be determined and expressed as a numerical value in appropriate units.

Qualitative analysis may take place without quantitative analysis, but quantitative analysis requires the identification (qualification) of the analyte.

Quantitative analysis can be divided into:-

1. Volumetric analysis
 - a. Titration method
 - b. Gas analysis method
2. Gravimetric analysis
 - a. direct method
 - b. indirect method
 - c. precipitation electrolysis

Gravimetric analysis:-

Is the quantitative isolation of a substance by precipitation and the weighing of the precipitate.

Gravimetric analysis involves determining the amount of material present by weighing the sample before and/or after some transformation. A common example is the determination of the amount of water in a hydrate by heating the sample to remove the water such that the difference in weight is due to the loss of water.

Volumetric analysis:-

1. The determination of the concentration, by volume, of a substance in a solution, as by titration.
2. The determination of the volume of gases or changes in their volume during combination.

Instrumental methods

Instrumental methods use an apparatus to measure physical quantities of the analyte such as light absorption, fluorescence, or conductivity. The separation of materials is accomplished using chromatography, electrophoresis or Field Flow Fractionation methods, (1) Spectroscopy, (2) Electrochemical analysis.

Types of error in analysis

1. Personal error
2. Operation error
3. Instrumental error
4. Random error, the error done and cannot be controlled by person like sudden change in electric and heat.

Standard solution

A standard solution is a solution containing a known concentration of an element or a substance. A known weight of solute is dissolved to make a specific volume, it is prepared using a standard substance, such as a primary standard. Standard solutions are used to determine the concentrations of other substances, such as solutions in titrations.

The concentrations of standard solutions are normally expressed in (mol/L), (mol/dm³), (kmol/m³) or normally in g.eqwt/L.

Uses

A solution of acid can be standardized by titrating it against a solution of alkali of known concentration. Once this has been calculated, it can in turn be used as a standard solution to find the concentration of a solution of alkali.

Standard solutions are also commonly used to determine the concentration of an analyte species.

Primary standard

A primary standard is a standard that is sufficiently accurate such that it is not calibrated by or subordinate to other standards. Primary standards are defined via

other quantities like length, mass and time. Primary standards are used to calibrate other standards referred to as working standards.

A primary standard is a reagent that is extremely pure, stable, has no waters of hydration, and has a high molecular weight.

Features of a primary standard include:

1. High purity
2. Stability (low reactivity)
3. Low hygroscopicity
4. High equivalent weight
5. Non-toxicity
6. Ready and cheap availability

Examples:

- Arsenic trioxide
- Benzoic acid
- Potassium bromate (KBrO_3)
- Potassium hydrogen phthalate
- Sodium carbonate for standardisation of aqueous acids: hydrochloric, sulfuric acid and nitric acid solutions (but not acetic acid)
- Sodium chloride for standardisation of silver nitrate solutions
- Sulfanilic acid for standardisation of sodium nitrite solutions
- Zinc powder after being dissolved in sulfuric or hydrochloric acid, for standardization of EDTA solutions

Such standards are often used to make standard solutions. Primary standards are used in titration and are essential for determining unknown concentrations or preparing working standards.

Solution

A **solution** is a homogeneous mixture composed of only one phase. In such a mixture, a **solute** is a substance dissolved in another substance, known as a solvent. The solvent does the dissolving. The concentration of a solute in a solution is a measure of how much of that solute is dissolved in the solvent.

Characteristics

- A solution is a homogeneous mixture
- The particles of solute in solution cannot be seen by naked eye.
- A solution is stable.
- The solute from the solution cannot be separated by filtration

Types

Homogeneous means that the components of the mixture form a single phase. The properties of the mixture (such as concentration, temperature, and density) can be uniformly distributed through the volume but only in absence of diffusion phenomena or after their completion. Usually, the substance present in the greatest amount is considered the solvent. Solvents can be gases, liquids or solids. One or more components present in the solution other than the solvent are called solutes. The solution has the same physical state as the solvent.

Gas

If the solvent is a gas, only gases are dissolved under a given set of conditions. An example of a gaseous solution is air (oxygen and other gases dissolved in nitrogen).

Liquid

If the solvent is a liquid, then gases, liquids, and solids can be dissolved. Here are some examples:

Gas in liquid:

- Oxygen in water
- Carbon dioxide in water a less simple example, because the solution is accompanied by a chemical reaction (formation of ions). Note also that the visible bubbles in carbonated water are not the dissolved gas, but only an effervescence of carbon dioxide that has come out of solution; the dissolved gas itself is not visible since it is dissolved on a molecular level.

Liquid in liquid:

- The mixing of two or more substances of the same chemistry but different concentrations to form a constant. (Homogenization of solutions).
- Alcoholic beverages are basically solutions of ethanol in water.

Solid in liquid:

- Sucrose (table sugar) in water
- Sodium chloride (table salt) or any other salt in water, which forms an electrolyte: When dissolving, salt dissociates into ions.

Counter examples are provided by liquid mixtures that are not homogeneous: colloids, suspensions, emulsions are not considered solutions.

Body fluids are examples for complex liquid solutions, containing many solutes. Many of these are electrolytes, since they contain solute ions, such as potassium. They contain solute molecules like sugar and urea. Oxygen and carbon dioxide are also essential components of blood chemistry, where significant changes in their concentrations may be a sign of severe illness or injury.

Solid

If the solvent is a solid, then gases, liquids and solids can be dissolved.

Gas in solids:

- Hydrogen dissolves rather well in metals, especially in palladium; this is studied as a means of hydrogen storage.

Liquid in solid:

- Mercury in gold, forming an amalgam
- Hexane in paraffin wax

Solid in solid:

- Steel, basically a solution of carbon atoms in a crystalline matrix of iron atoms.
- Alloys like bronze and many others.
- Polymers containing plasticizers.

Solubility

The ability of one compound to dissolve in another compound is called solubility, When a liquid can completely dissolve in another liquid the two liquids are miscible. Two substances that can never mix to form a solution are called immiscible.

All solutions have positive entropy of mixing. The interactions between different molecules or ions may be energetically favored or not. If interactions are unfavorable, then the free energy decreases with increasing solute concentration. At some point the energy loss outweighs the entropy gain, and no more solute particles can be dissolved; the solution is said to be

Saturated solutions the point at which a solution can become saturated can change significantly with different environmental factors, such as temperature, pressure, and contamination, For some solute-solvent combinations **a supersaturated solution**

can be prepared by raising the solubility (for example by increasing the temperature) to dissolve more solute, and then lowering it (for example by cooling).

Usually, the greater the temperature of the solvent, the more of a given solid solute it can dissolve. However, most gases and some compounds exhibit solubility that decrease with increased temperature. Such behavior is a result of an exothermic enthalpy of solution. Some surfactants exhibit this behavior. The solubility of liquids in liquids is generally less temperature-sensitive than that of solids or gases.

Properties

The physical properties of compounds such as melting point and boiling point change when other compounds are added. Together they are called colligative properties. There are several ways to quantify the amount of one compound dissolved in the other compounds collectively called concentration. Examples include molarity, mole fraction, and parts per million (PPM).

The properties of ideal solutions can be calculated by the linear combination of the properties of its components. If both solute and solvent exist in equal quantities (such as in a 50% ethanol, 50% water solution), the concepts of "solute" and "solvent" become less relevant, but the substance that is more often used as a solvent is normally designated as the solvent (in this example, water).

Liquid

In principle, all types of liquids can behave as solvents. They can be classified into polar and non-polar, according to whether their molecules possess a permanent electric dipole moment.

Another distinction is whether their molecules can form hydrogen bonds.

Water, the most commonly used solvent, is both polar and sustains hydrogen bonds. Water is a good solvent because the molecules are polar and capable of forming hydrogen bonds.

Salts dissolve in polar solvents, forming positive and negative ions that are attracted to the negative and positive ends of the solvent molecule, respectively. If the solvent is water, hydration occurs when the charged solute ions become surrounded by water molecules. A standard example is aqueous saltwater. Such solutions are called electrolytes.)

For non-ionic solutes, the general rule is: **like dissolves like**.

Polar solutes dissolve in polar solvents, forming polar bonds or hydrogen bonds. As an example, all alcoholic beverages are aqueous solutions of ethanol. On the other hand, non-polar solutes dissolve better in non-polar solvents. Examples are hydrocarbons such as oil and grease that easily mix with each other, while being incompatible with water.

An example for the immiscibility of oil and water is a leak of petroleum from a damaged tanker that does not dissolve in the ocean water but rather floats on the surface.

Concentration (conc.)

The amount of solute dissolved in amount of solvent to form the solution. There are many ways to express the conc.

1. Solid substance

- Molarity
- Normality
- Percentage
- parts per Million or Billion

Molarity (M)

It is the number of grams molecular weight (mole) of solute dissolved in 1 liter of solution. Unit of molarity (mole / L)

$$\text{Molarity (M)} = \frac{\text{No. of moles of solute}}{\text{vol. liters solution}}$$

$$M = \frac{\text{Gram of solute}}{\text{Molecular weight}} \times \frac{1000}{V \text{ (ml)}} \rightarrow \text{for solid in liquid}$$

$$\text{Molecular Weight (M.Wt)} = \sum \text{Atomic weight}$$

الوزن الجزيئي = مجموع الاوزان الذرية

E.X 1 : What is the molarity of a solution that contains 1.724 moles of H₂SO₄ in 2.5 L of solution?

$$\text{Molarity (M)} = \frac{1.724 \text{ mol}}{2.5 \text{ L}} = 0.690 \text{ M H}_2\text{SO}_4$$

E.X 2 : A 4 g sugar cube (sucrose C₁₂H₂₂O₁₁) is dissolved in a 350 ml tea cup filled with hot water. What is the molarity of the sugar solution? If you know (C=12, O= 16 , H=1) g/mol

M.wt of sucrose $C_{12}H_{22}O_{11} = [(12 \times 12) + (1 \times 22) + (16 \times 11)] = 342 \text{ g/mol}$

No. of moles of sucrose $C_{12}H_{22}O_{11} = \frac{Wt}{M.wt} = \frac{4}{342} = 0.0117 \text{ mol}$

Molarity (M) = $\frac{\text{No. of moles of solute}}{\text{vol. liters solution}} = \frac{0.0117}{0.350 \text{ L}} = 0.033 \text{ mol/L}$

E.X 3: Prepare one molar solution of Na_2CO_3 in 1 L (A.wt for Na= 23, C=12,O=16) g/mol

M.wt. $Na_2CO_3 = [23 \times 2 + 12 + 3 \times 16] = 106 \text{ g/mol}$

$$M = \frac{wt}{M.wt} \times \frac{1000}{V (ml)}$$

$$1 = \frac{wt}{106} \times \frac{1000}{1000(ml)}$$

Wt = 106 g

Normality (N)

It is the number of gram equivalent weight of solute dissolved in one liter of solution.

Unit of normality (g.eq.wt / L)

Normality (N) = $\frac{\text{No. of eq. moles of solute}}{\text{vol. liters solution}}$

$N = \frac{wt}{Eq. wt} \times \frac{1000}{V (ml)}$ → for solid in liquid

Calculation of Equivalent Weight

$$1- \text{equivalent weight for acid} = \frac{\text{molecular weight}}{\text{number of hydrogen atoms}}$$

$$(\text{eq.wt of H}_2\text{SO}_4) = 98/2 = 49 \text{ g/eq}$$

$$2- \text{equivalent weight for base} = \frac{\text{molecular weight}}{\text{number of hydroxyl atoms}}$$

$$(\text{eq.wt of NaOH}) = 40/1 = 40 \text{ g/eq}$$

$$3- \text{equivalent weight for salt} = \frac{\text{molecular weight}}{\text{total oxidation no.of metal}}$$

$$(\text{eq.wt of NaCl}) = 58.5/1 = 58.5 \text{ g/eq}$$

H.W : prepare 0.12 N of NaCl in 250 ml , At.wt (Na = 23 , Cl = 35.5) g /mol

2- Liquid substances:

A. Molarity

B. Normality

C. Percentage

Normality and Molarity of strong acid or liquids

The table of strong acid give the following information:

Acid	Sp.gr	%
HCl	1.19	37.9
H ₂ SO ₄	1.84	96.0
HNO ₃	1.82	69.8

$$M = \frac{\% \times \text{sp. gr.} \times 1000}{\text{M. wt}} = \frac{\% \times d \times 1000}{\text{M. wt}} \quad \rightarrow \text{for liquid in liquid}$$

$$N = \frac{\% \times \text{sp. gr.} \times 1000}{\text{eq. wt}} = \frac{\% \times d \times 1000}{\text{eq. wt}} \quad \rightarrow \text{for liquid in liquid}$$

Density : Is the ratio of mass of material to its volume . Unit of density gm/ml

$$D = \frac{\text{Mass of material (gm)}}{\text{Volume (ml)}} = \text{gm/cm}^3$$

Specific gravity (sp. Gr.):

Is the ratio of density of any material to the density of water (without unit)

$$\text{Sp. gr} = \frac{\text{density of material}(\frac{\text{gm}}{\text{ml}})}{\text{density of water}(\frac{\text{gm}}{\text{ml}})}$$

Density of water(d) = 1gm/ml (always)

E.X / prepare (0.1 N in 500 ml of solution of Hydrochloric Acid (HCl) from concentration solution. if you know: Sp. Gr. 1.19, percentage ratio 37.9% and A.Wt. H=1 Cl=35.5

Solution:-

M.wt of HCl = 35.5 + 1 = 36.5 g / mol

Eq.wt = 36.5 / 1 = 36.5 g / eq

$$N = \frac{\% \times \text{sp. gr.} \times 1000}{\text{eq. wt}} = \frac{\frac{37.9}{100} \times 1.19 \times 1000}{36.5} = 12.3 \text{ g. eq. wt/L}$$

$$(N_1 \times V_1)_{\text{conc.}} = (N_2 \times V_2)_{\text{dilu.}}$$

$$12.3 \times V_1 = 0.1 \times 500$$

$V_1 = 4.06$ ml to be complete to 500 ml H_2O .

Percentage

a. Weight by weight

$$W/W \% = \frac{\text{wt of solute}}{\text{wt of solution}} \times 100$$

b. Volume by volume

$$V/V \% = \frac{V \text{ of solute}}{V \text{ of solution}} \times 100$$

C. Weight by Volume

$$W / V\% = \frac{\text{wt of solute}}{V \text{ of solution}} \times 100$$

E.X : Prepare a standard solution of NaCl (2%) in 250 ml in D.W.

$$W / V\% = \frac{\text{wt of solute}}{V \text{ of solution}} \times 100$$

$$2 = \frac{\text{wt of solute}}{250} \times 100 = \quad \text{wt} = 5 \text{ gm}$$

Concentration in parts per Million or Billion:

$$\text{part per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

$$\text{part per billion (ppb)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^9$$

Dilution

The process of making a substance less concentrated by adding a solvent , such as water.

$$C_1 V_1 = C_2 V_2$$

$$M_1 V_1 = M_2 V_2$$

$$N_1 V_1 = N_2 V_2$$

H.W / Prepare 3% of KMnO_4 in 100 ml and dilute to 2% and 0.4 % and 0.05 % in 100 ml for each.

Neutralization reactions

In chemistry, neutralization is a chemical reaction in which an acid and a base react to form a salt. Water is frequently, but not necessarily, produced as well. Neutralization reactions are exothermic

Arrhenius acids and bases

Svante Arrhenius defined an acid as a substances that produces hydrogen ions, or protons (H^+) in aqueous solutions.

common examples of Arrhenius acids because



Arrhenius defined a base as a substance that produces hydroxide (OH^-) in aqueous solutions. Arrhenius's definition of a base was limited because along with produced hydroxide ions in solution, the base must contain the hydroxide group in its formula. Potassium hydroxide (KOH) and caesium hydroxide (CSOH) are common examples of Arrhenius bases because, when they dissociate into their ions, they increase the amount of OH^- in the solution:



Net ionic equation

When an acid reacts with an equal amount of a base, the word "**neutralization**" is used to describe the result because the acid and base properties of H^+ and OH^- are destroyed or neutralized. In the reaction, H^+ and OH^- combine to form HOH^- more commonly written as H_2O , the water molecule. Thus, acid-base neutralization reactions can be simplified to the net ionic equation: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

It is important to realize that the hydrogen ion (H^+) does not actually occur by itself, but instead as the hydronium ion (H_3O^+). As seen in the following reaction, the H^+ , or protons, cause molecules of water undergo protonation to form the hydronium ion:



Considering the hydronium ion, the actual net ionic reaction occurring is:

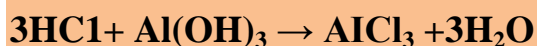
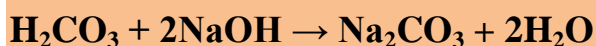


General neutralization equation

A neutralization reaction is a type of double replacement reaction. The general formula for acid-base neutralization reactions can be written as:



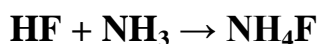
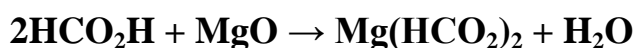
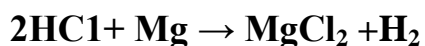
The following are other examples of acid-base neutralization reactions



Non-aqueous reactions

In non-aqueous reactions, water is less likely to be formed; however, there is always a donation of protons. All of the following may be considered neutralization reactions under different definitions:





Resultant pH

Neutralization reactions do not necessarily imply a resultant pH of 7. In the case that

1- Strong acid and strong base

participate in a neutralization reaction, the resultant pH will be 7.



2- Weak acid and a strong base

participate in a neutralization reaction, the resultant pH will be greater than 7.

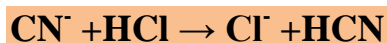


Na^+ behaves as a spectator ion. However, acetate is a weak base that hydrolyzes water to give OH^- ions.



3- Weak base and a strong acid

participate in a neutralization reaction, the resultant pH will be less than 7.



Cl^- behaves as a spectator ion. However, hydrocyanic acid is a weak acid that hydrolyzes water to give H_3O^+ ions.



4- Weak acid and a weak base

participate in a neutralization reaction, the resultant pH will depend on the relative strength of the acid and base reactants.



Because CH_3COOH ($\text{pK}_a = 4.75$) is a stronger acid than HCN ($\text{pK}_a = 9.2$), the equilibrium is driven to the right.

The acetate ions then react with water to give acetic acid and OH^-



The resultant solution is basic. However, this is not a general rule for all neutralization reactions between a weak acid and a weak base.

Chemical titration methods are used for analyzing acids or bases to determine the unknown concentration. And can use a pH meter or a pH indicator which shows the point of neutralization. The neutralization reactions are used when food is moved from the stomach to the intestines. In order for the nutrients to be absorbed through the intestinal wall, an alkaline environment is needed, so the pancreas produces antacid bicarbonate to cause this transformation to occur.

Titration

Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified analyte. Since volume measurements play a key role in titration, it is also known as **volumetric analysis**. A reagent, called the titrant or titrator is prepared as a standard solution, A known concentration and volume of titrant reacts with a solution of analyte or titrand to determine concentration.

Buffer solution

The PH value of NaCl solution & CH_3COONa is 7, if 1cm^3 of 0.1N (HCl) solution is added to each solution the PH of NaCl will change from 7 to 4. While the PH of (CH_3COONa) remains 7.

IF 1 cm^3 of (NaOH) solution (0.1N) added to both solutions, the PH of NaCl will change to 10.

While the PH of other solution (CH_3COONa) remains 7. So we find that solution CH_3COONa resist the change in PH when either acid or base is added, this characteristic is called buffer action.

Buffer Solution:

Defined as solution with constant hydrogen ion concentration and can resist any change in PH when moderate amount of acid or base were added.

Why buffer contains a mixture of acid and base?

Buffer solution consists always of a mixture of acid and base in order to have the ability to resist the effect of both acid & base.

Buffer solution is prepared from weak acid & its salt with strong base, or weak base & its salt with strong acid.

PH Value

The negative logarithm is PH value problems of hydrogen ion activity in the problems. We are in general neglecting activity value.

POH value is the negative logarithm of hydroxyl ion (anion).

$$\text{PH} = -\log [\text{H}^+] \text{ or } [\text{H}_3\text{O}^+]$$

$$\text{POH} = -\log [\text{OH}^-]$$

The pH value of pure water at 25°C is 7.0

The pH value of acid Solution is less than 7.0

The pH value of alkaline solution is greater than 7.0

In general at 25°C

$$\text{PH} + \text{POH} = 14$$

$$[\text{H}^+] [\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

$$[\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]}$$

E.X₁ / what is the pH value and [OH⁻] of a Solution that is 0.001 M in HCl?

Solution:

$$[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$$

$$\text{PH} = -\log (1.0 \times 10^{-3})$$

$$\text{PH} = 3 - \log 1$$

$$\text{PH} = 3$$

$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-3}} = 10^{-11} \text{ M}$$

E.X₂ /The PH value of Solution is (5.92). What are the POH value, the hydrogen ion Conc. and the hydroxyl ion Conc.?

Solution:

$$\text{POH} = 14 - 5.92 = 8.08$$

$$[\text{H}^+] = 10^{-5.92} \times 10^6 \times 10^{-6}$$

$$[\text{H}^+] = 10^{0.08} \times 10^{-6}$$

$$[\text{H}^+] = 1.2 \times 10^{-6} \text{ M}$$

$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{1.2 \times 10^{-6}} = 0.83 \times 10^{-8} \text{ M}$$

Reliability of Analytical Data

Error in chemical Analysis

The error observed value and the true value in any chemical analysis is related by an equation.

$$E = (O-T)$$

E = absolute error

O = observed value

T = true value

Usually the error of measurement is an inverse measure of accuracy of that measurement is an inverse measure of accuracy of that measurement.

The error are generally expressed relatively as percentage errors (R)

$$\text{Percentage} = \frac{E}{T} \times 100 = \% \text{ error}$$

$$\text{Perthousand} = \frac{E}{T} \times 1000 = \text{ppt}$$

Classification of error:

The errors are classified in to two groups namely determinate error and indeterminate errors, the determinate errors are those errors which are having definite values, whereas the in determinate errors are those which possess indefinite values and no law and no invariably have fluctuating values. The determinate errors are of three kinds depending upon their origin, namely, methodic, operative and instrumental in nature.

Statistical Analysis

1. Absolute and relative difference in the values
2. Mean (\bar{x}) value and deviation (D)
3. Average deviation (d) of single measurements
4. Average deviation of mean
5. Standard deviation (s)
6. Standard deviation of means (d)
7. Median value
8. Relative standard deviation

Mean (\bar{x}) or arithmetical mean or average that refer to the numerical value obtained by dividing the sum (Σ) of asset of replicate measurements by number of individual resulting the set.

$$\bar{x} = \frac{X_1 + X_2 + \dots + X_n}{n} = \frac{\Sigma X_i}{n}$$

حيث n عدد مرات اعادة التجربة

Median الوسيط

Is that result, which all of the other are equally distributed, half being numerically greater and half numerically smaller.

Calculate the median and mean for 10.06, 10.20, 10.08,10.10

$$\bar{x} = \frac{10.06 + 10.20 + 10.08 + 10.10}{4} = 10.11$$

Because the set contains an even number of measurement, the median is the average of the middle pair.

$$\text{Median} = \frac{10.08 + 10.10}{2} = 10.09$$

إذا كان عدد الأرقام فردي فيؤخذ وسط هذه الأرقام أما إذا كان زوجي فيؤخذ متوسط العدد بين الوسطين

Accuracy **الدقة**

The term (accuracy) denotes the nearness of measurement to its accepted value.

مدى التقارب بين القيم العددية للقياسات عند تكرارها

Standard deviation (d or σ)

الانحراف القياسي

طريقة حساسة للنتائج التي تبتعد عن الوسط الحسابي

Is precise measure and is reliable measure of deviation

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

يهمل ال 1 في عدد كبير من التجارب

n = the number of data point

X_i = each of the values of the data

\bar{x} = the mean of **X_i**

القيمة الموجبة للجذر التربيعي لمجموع مربعات انحراف القيم العددية للقراءات عن وسطها الحسابي مقسوما على عدد القياسات n-1

Average Deviation (d)

متوسط الانحراف للقراءة الواحدة

Average deviation of a single measurement is the mean of the deviation of all the individual measurement.

$$d = \frac{\sum |X_i - X|}{n}$$

Deviation (D) المعدل

Is equal to the average deviation of single measurement deviated by square root of the number of measurements

$$D = \frac{d}{\sqrt{n}}$$

Relative standard deviation (R.S.D) الانحراف القياسي النسبي

$$R. S. D = \frac{S}{\bar{x}} \times 100$$

Oxidizing and reducing agents

In redox processes, the reductant transfers electrons to the oxidant. Thus, in the reaction, the reductant or reducing agent loses electrons and is oxidized, and the oxidant or oxidizing agent gains electrons and is reduced.

The pair of an oxidizing and reducing agent that are involved in a particular reaction is called a **redox pair**. A **redox couple** is a reducing species and its corresponding oxidized form, e.g., $\text{Fe}^{+2}/\text{Fe}^{+3}$.

Oxidizers (oxidizing agent)

Substances that have the ability to oxidize other substances, it removes electrons from another substance, and is thus it self-reduced. And, because it "accepts" electrons, the oxidizing agent is also called an electron acceptor.

Oxidants are usually chemical substances with elements in high oxidation states (e.g. H_2O_2 , MnO^{-4} , CrO_3 , $\text{Cr}_2\text{O}_2^{-7}$, OsO_4) or else highly electronegative elements (O_2 , F_2 , Cl_2 , Br_2) that can gain extra electrons by oxidizing another substance.

Reducers (Reducing agent)

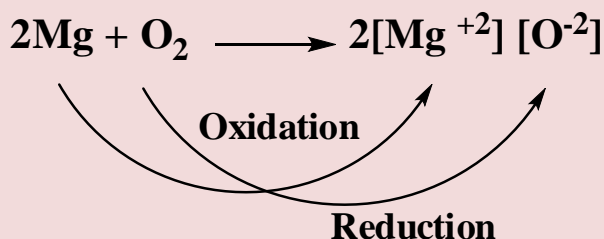
Substances that have the ability to **reduce** other substances, its (reducing agent) transfers electrons to another substance, and are thus it self-oxidized. And, because it "donates" electrons, the reducing agent is also called an electron donor.

Reductants in chemistry are very diverse. Electropositive elemental metals, such as lithium, sodium, magnesium, iron, zinc, and aluminum, are good reducing agents. These metals donate or give away electrons readily.

Hydride transfer reagents, such as NaBH_4 , and LiAlH_4 , are widely used in organic chemistry.

Magnesium metal, for example, was thought to lose electrons to form Mg ions when it reacted with oxygen. By convention, the element or compound that gained these

electrons was said to undergo **reduction**. In this case O_2 molecules were said to be reduced to form O^{-2} ions.



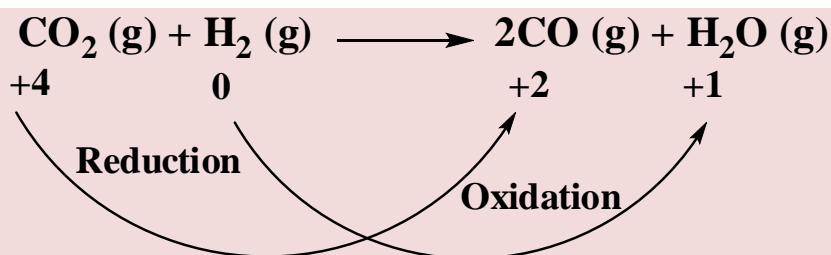
A classic demonstration of oxidation-reduction reactions involves placing a piece of copper wire into an aqueous solution of the Ag^+ ion. The reaction involves the net transfer of electrons from copper metal to Ag^+ ions to produce whiskers of silver metal that grow out from the copper wire and Cu^{+2} ions.



The Cu^{+2} ions formed in this reaction are responsible for the light-blue color of the solution. Their presence can be confirmed by adding ammonia to this solution to form the deep-blue $Cu(NH_3)_4^{+2}$ complex ion.

Oxidation involves an increase in the oxidation number of an atom. Reduction occurs when the oxidation number of an atom decreases.

According to this model, CO_2 is reduced when it reacts with hydrogen because the oxidation number of the carbon decreases from +4 to +2. Hydrogen is oxidized in this reaction because its oxidation number increases from 0 to +1.



Examples of redox reactions

A good example is the reaction between hydrogen and fluorine in which hydrogen is being oxidized and fluorine is being reduced:



We can write this overall reaction as two half-reactions:

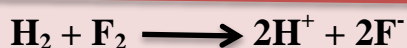


Analyzing each half-reaction in isolation can often make the overall chemical process clearer. Because there is no net change in charge during a redox reaction, the number of electrons in excess in the oxidation reaction must equal the number consumed by the reduction reaction (as shown above).

Elements, even in molecular form, always have an oxidation state of zero. In the first half-reaction, hydrogen is oxidized from an oxidation state of zero to an oxidation state of +1.

In the second half-reaction, fluorine is reduced from an oxidation state of oxidation state of -1.

When adding the reactions together the electrons are canceled:



And the ions combine to form hydrogen fluoride:

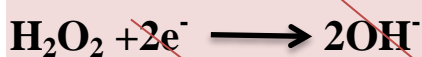
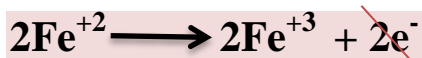


The overall reaction is:



Other examples

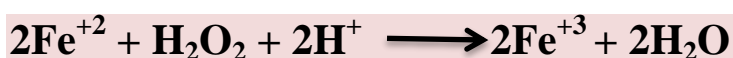
The oxidation of iron(II) to iron(III) by hydrogen peroxide in the presence of an acid:



In acid medium (H^{+})

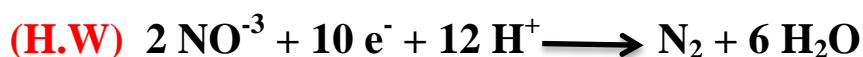


Overall equation:



The reduction of nitrate to nitrogen in the presence of an acid

(denitrification)



Balancing redox reactions

Describing the overall electrochemical reaction for a redox process requires a balancing of the component half-reactions for oxidation and reduction. In general, for reactions in aqueous solution, this involves adding H^{+} , OH^{-} , H_2O , and electrons to compensate for the oxidation changes.

Acidic media

In acidic media, H^{+} ions and water are added to half-reactions to balance the overall reaction. For instance, when manganese (II) reacts with sodium bismuthate:

Unbalanced reaction:



Oxidation:

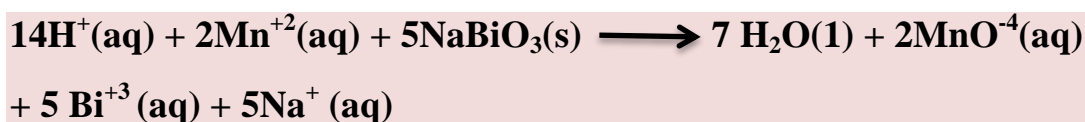


Reduction:

The reaction is balanced by scaling the two half-cell reactions to involve the same number of electrons (multiplying the oxidation reaction by the number of electrons in the reduction step and vice versa):

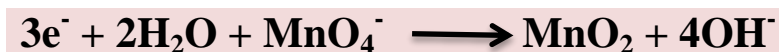


Adding these two reactions eliminates the electrons terms and yields the balanced reaction:

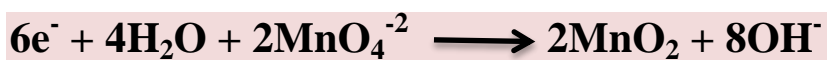
**Basic media**

In basic media, OH^- ions and water are added to half reactions to balance the overall reaction.

For example, in the reaction between potassium permanganate and sodium sulfite:

Unbalanced reaction:**Reduction:****Oxidation:**

Balancing the number of electrons in the two half-cell reactions gives:



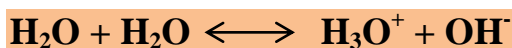
Adding these two half-cell reactions together gives the balanced equation:



Self-ionization of water (auto ionization of water)

The **self-ionization of water** is an ionization reaction in pure water that loses the nucleus of one of its hydrogen atoms to become a hydroxide ion, OH^- . The hydrogen nucleus, H^+ , immediately protonates another water molecule to form hydronium, H_3O^+ .

Equilibrium constant Chemically pure water has an electrical conductivity of $0.055 \mu\text{S cm}^{-1}$. According to the theories of Svante Arrhenius, this must be due to the presence of ions. The ions are produced by the self- ionization reaction



This equilibrium applies to pure water and any aqueous solution.

The chemical equilibrium constant, K_{eq} , for this reaction is given by:

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The ionization constant of water, symbolized by K_{w} may be given by:

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_{\text{eq}} \times [\text{H}_2\text{O}]^2$$

Where $[\text{H}_3\text{O}^+]$ is the concentration of hydrogen or hydronium ion, and $[\text{OH}^-]$ is the concentration of hydroxide ion.

At 25°C K_{w} is equal to 1.0×10^{-14}

Ionization of Water

The water can act as a very weak acid and a very weak base, donating protons to itself to a limited extent:



Applying the equilibrium law to this reaction, we obtain

$$K_C = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The concentration of water has a constant value of 55.5 mol dm^{-3} , and so its square can be multiplied by K_C to give a new constant K_W called the ion product constant of water:

$$K_W = K_C \times (55.5 \text{ mol dm}^{-3})^2 = [\text{H}_3\text{O}^+][\text{OH}^-] \dots(1)$$

Measurements of the electrical conductivity of carefully purified water indicate that at 25°C $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$ so that

$$\begin{aligned} K_W &= 1.00 \times 10^{-7} \text{ mol dm}^{-3} \times 1.00 \times 10^{-7} \text{ mol dm}^{-3} \\ &= 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6} \end{aligned}$$

(Since the equilibrium law is not obeyed exactly, even in dilute solutions, results of most equilibrium calculations are rounded to three significant figures. Hence the value of $K_W = 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6}$ is sufficiently accurate for all such calculations.)

The equilibrium constant K_W applies not only to pure water but to any aqueous solution at 25°C . Thus, for example, if we add 1.00 mol of the strong acid HNO_3 to H_2O to make a total volume of 1 dm^3 essentially all the HNO_3 molecules donate their protons to H_2O :



and a solution in which $[\text{H}_3\text{O}^+] = 1.00 \text{ mol dm}^{-3}$ is obtained. Although this solution is very acidic, there are still hydroxide ions present. We can calculate their concentration by rearranging Eq. (1):

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{1.00 \text{ mol dm}^{-3}}$$

$$= 1.00 \times 10^{-14} \text{ mol dm}^{-3}$$

The addition of the HNO_3 to H_2O not only increases the hydronium-ion concentration but also reduces the hydroxide-ion concentration from an initially minute $10^{-7} \text{ mol dm}^{-3}$ to an even more minute $10^{-14} \text{ mol dm}^{-3}$.

EXAMPLE

Calculate the hydronium-ion concentration in a solution of 0.306 M $\text{Ba}(\text{OH})_2$.

Solution Since 1 mol $\text{Ba}(\text{OH})_2$ produces 2 mol OH^- in solution, we have

$$[\text{OH}^-] = 2 \times 0.306 \text{ mol dm}^{-3} = 0.612 \text{ mol dm}^{-3}$$

Then

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{0.612 \text{ mol dm}^{-3}}$$

$$= 1.63 \times 10^{-14} \text{ mol dm}^{-3}$$

Note that since strong acids like HNO_3 are completely converted to H_3O^+ in aqueous solution, it is a simple matter to determine $[\text{H}_3\text{O}^+]$, and from it, $[\text{OH}^-]$.

Similarly, when a strong base dissolves in H_2O it is entirely converted to OH^- , so that $[\text{OH}^-]$, and from it $[\text{H}_3\text{O}^+]$ are easily .