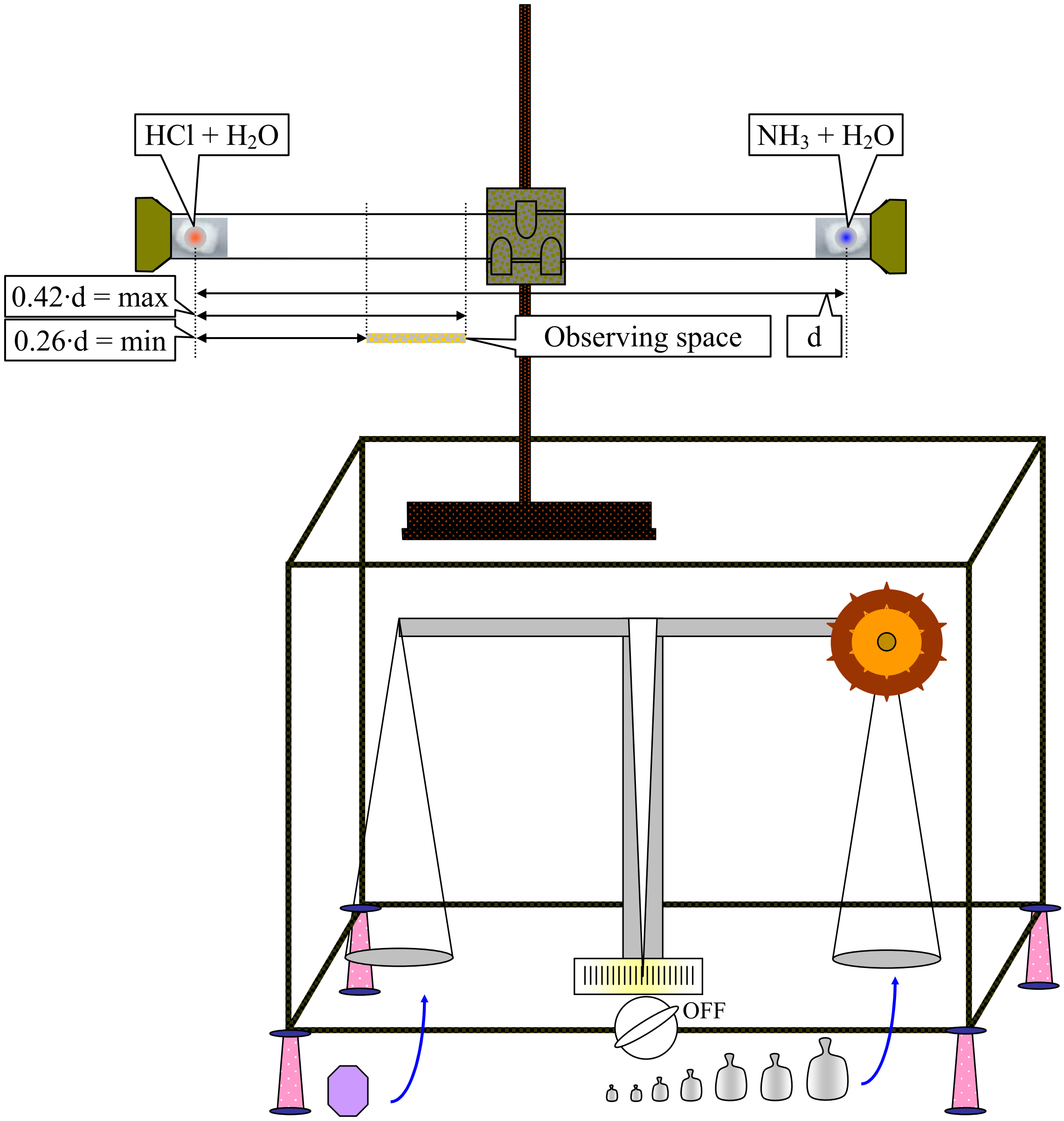
General chemistry laboratory activities

Lorentz JÄNTSCHI
Sorana D. BOLBOACĂ



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Introduction

This is the first version of the new plan (and very probably will be revised shortly after its first year of operation) for conducting the laboratory activities at General chemistry and is addressed especially for the students having Chemistry discipline for only one semester of study. The activities to be conducted in the laboratory were specifically designed to be applied for the students in the followings fields of study: Robotics, Industrial engineering, Economical engineering and Vehicles engineering.

March 20, 2015

Contents

Laboratory glassware

Introduction

This chapter is intended to accommodate with the laboratory glassware. Other sources which may be consulted are [[1]], [[2]], [[3]], [[4]], and [[5]].

Test tubes and common flasks

A test tube (or culture tube or sample tube) is a common piece of laboratory glassware consisting of a finger-like length (also available in a multitude of lengths and widths, typically of 10-20 mm wide and 50-200 mm long) of glass or clear plastic tubing, open at the top.

Test tubes are widely used by chemists to hold, mix, or heat small quantities of solid or liquid chemicals, especially for qualitative experiments and assays. Their round bottom and straight sides minimize mass loss when pouring, make them easier to clean, and allow convenient monitoring of the contents. The long, narrow neck slows down the spreading of vapours and gases to the environment.

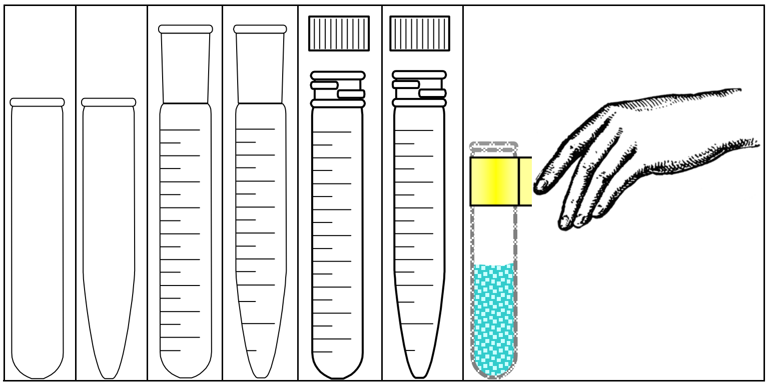


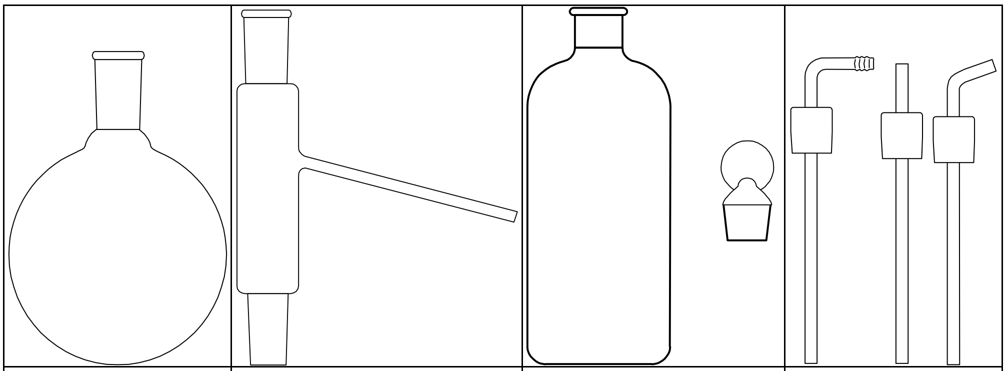
Figure 1. Test tubes with different construction and manipulating with a paper sleeve

When manipulating test tubes, following statements are useful to be considered (see Figure 1):

- Test tubes serves to conduct chemical reactions for testing;
- Have a cylindrical shape and are closed at one end and it may be graduated;
- Usually are filled no more than half of their length;
- When heated are held with a paper sleeve;
- The content is mixed with shaking;
- Is avoided to expose the opening of the tube to itself or to the persons around;
- When is heated is preferable to tilting it slightly to avoid sudden release of vapours;

Laboratory flasks are vessels (containers) which in laboratory and other scientific settings, they are usually referred to simply as flasks. Flasks come in a number of shapes and a wide range of sizes which are specified by the volume they can hold, typically in metric units such as millilitres (mL) or litres (L). Laboratory flasks have traditionally been made of glass, but can also be made of plastic.

Flasks are used for making solutions or for holding, containing, collecting, or sometimes volumetrically measuring chemicals, samples and solutions. Other applications include conducting of chemical reactions or other processes such as mixing, heating, cooling, dissolving, precipitation, boiling (as in distillation), or analysis.



Reaction flask | Distillation arm | Reagent flask | Glass tubing

Figure 2. Reaction flask, distillation arm, reagent flask, and glass tubing

Reaction flasks (see Figure 2) are usually spherical (i.e. round-bottom flask) and are accompanied by their necks, at the ends of which are ground glass joints to quickly and tightly connect to the rest of the apparatus (such as a reflux condenser or dropping funnel). The reaction flask is usually made of thick glass and they can tolerate large pressure differences, with the result that you can keep two both in a reaction under vacuum, and pressure, sometimes simultaneously. Varieties include multiple neck flasks (can have two to five, or less commonly, six necks, each topped by ground glass connections) being used in more complex reactions that require the controlled mixing of multiple reagents. Other variety is the Schlenk flask, being a spherical flask with a ground glass opening and a hose outlet with a vacuum stopcock. The tap makes it easy to connect the flask to a vacuum-nitrogen line through the hose and carrying out the reaction either in vacuum or in nitrogen.

Distillation flasks (see Figure 2) are intended to contain mixtures, which are subject to distillation, as well as to receive the products of distillation. Distillation flasks are available in various shapes. Similar to the reaction flask, the distillation flasks usually have only one narrow neck and a ground glass joint and are made of thinner glass than the reaction flask, so that it is easier to heat. An alternative is to use the distillation arms (see Figure 2).

Reagent flasks (see Figure 2) are usually a flat-bottomed flask, which can thus be conveniently placed on the table or in a cabinet. These flasks cannot withstand too much pressure or temperature differences, due to the stresses which arise in a flat bottom, these flasks are usually made of weaker glass than reaction flasks. Certain types of flasks are supplied with a ground glass stopper in them, and others that are threaded neck and closed with an appropriate nut or automatic dispenser.

Glass tubing (see Figure 2) is to be connected with a flask when gas flows or liquid flows are necessary to be controlled at certain pressure.

Erlenmeyer flask (see Figure 3) was introduced in 1861 by German chemist Emil Erlenmeyer (1825 -1909) and is shaped like a cone, usually completed by the ground joint.

Dewar flask (see Figure 3) was introduced in 1892 by Scottish chemist Sir James Dewar (1842 - 1923) and is a double-walled flask having a near-vacuum between the two walls. These come in a variety of shapes and sizes; some are large and tube-like, others are shaped like regular flasks.

Evaporating flasks (see Figure 3) are pear shaped, with socket or with flange, and are to be used with rotary evaporator.

Separation funnels (see Figure 3) are used in liquid-liquid extractions to separate (partition) the components of a mixture into two immiscible solvent phases of different polarities (typically, one of the phases will be aqueous, and the other a non-polar lipophilic organic solvent such as ether, MTBE, dichloromethane, chloroform, or ethyl acetate).

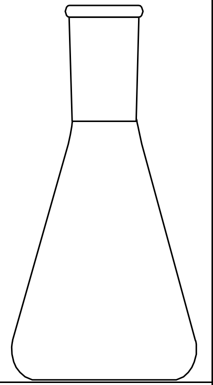
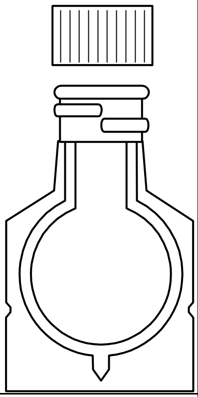
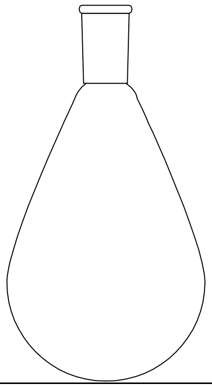
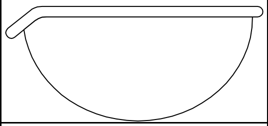
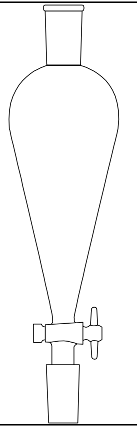
				
Erlenmeyer flask	Dewar flask	Evaporating flask	Evaporating dish	Separation funnel

Figure 3. Erlenmeyer flask, Dewar flask, Evaporating flask and dish, and Separation flask

Filtering flasks (see Figure 4) are to be used together with Büchner funnels (see Figure 4), void producing devices (see Figure 4), all mounted to a water tap (see Figure 4) to separate precipitates from liquids (also by using a filter paper).

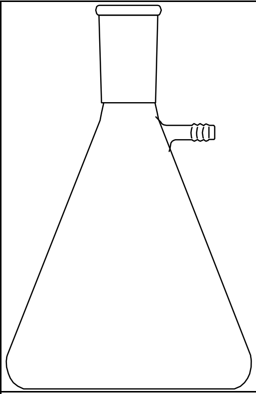
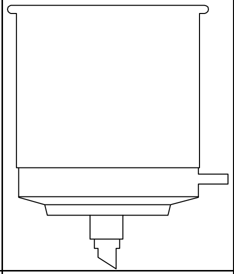
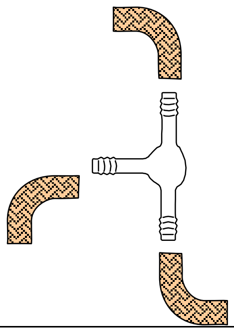
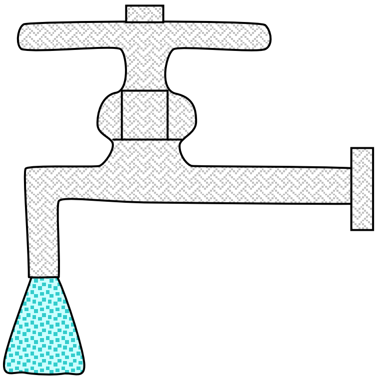
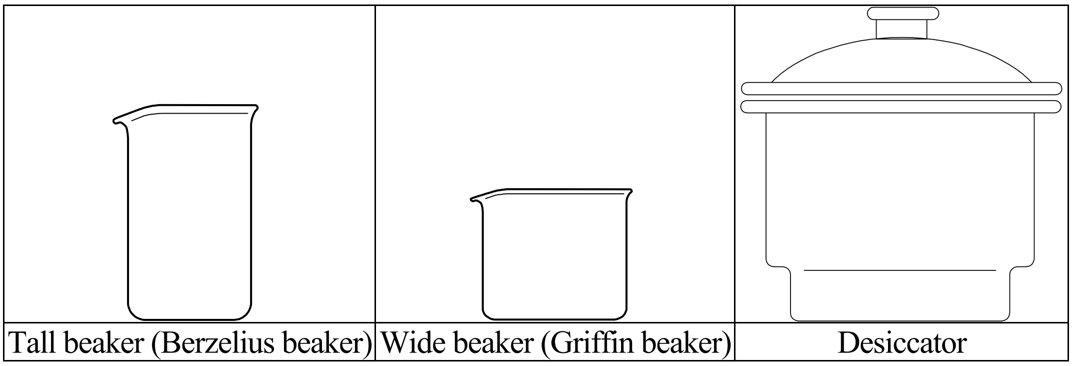
			
Filtering flask	Büchner funnel	Void producing device	Water tap

Figure 4. Filtering flask, Büchner funnel, Void producing device, Water tap

Filtering flask is a thick-walled Erlenmeyer flask with a short glass tube and hose barb protruding about an inch from its neck. The short tube and hose barb effectively acts as an adapter over which the end of a thick-walled flexible hose (tubing) can be fitted to form a connection to the flask. The other end of the hose can be connected to source of vacuum such as an aspirator, vacuum pump, or house vacuum. Preferably this is done through a trap, which is designed to prevent the sucking back of water from the aspirator into the flask.

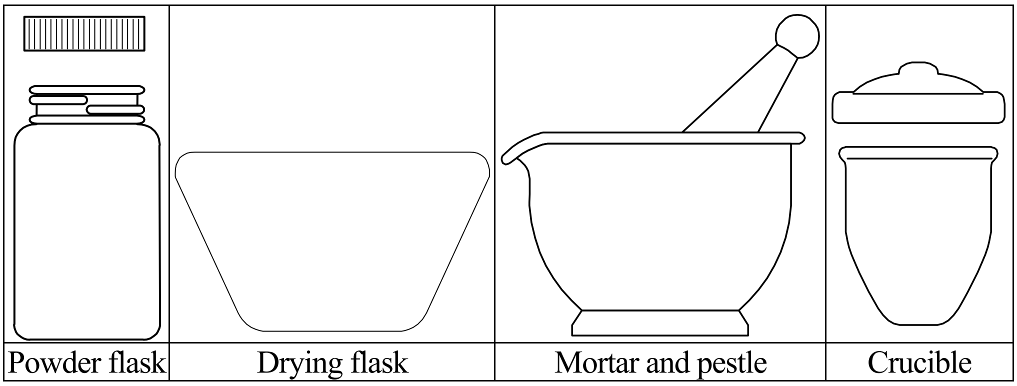


Tall beaker (Berzelius beaker) | Wide beaker (Griffin beaker) | Desiccator

Figure 5. Beakers (Berzelius and Griffin) and desiccator

A beaker (see Figure 5) is a simple container for stirring, mixing and heating liquids commonly used in many laboratories. Beakers are generally cylindrical in shape, with a flat bottom. The wide low form with a spout was devised by John Joseph Griffin and is therefore sometimes called a Griffin beaker. Tall-form beakers (have a height about twice the diameter) were devised by Jöns Jacob Berzelius and are therefore sometimes called Berzelius beakers and are mostly used for titration.

Desiccators (see Figure 5) are sealable enclosures containing desiccants preserving moisture-sensitive items (such as $CoCl_2$ paper) for another use. A common use for desiccators is to protect chemicals which are hygroscopic or which react with water from humidity.



Powder flask | Drying flask | Mortar and pestle | Crucible

Figure 6. Laboratory glassware and porcelain ware to be used for solids

Powder flasks (see Figure 6) are for keeping or drying of powdered substances, mortar and pestle (see Figure 6) for crumbling the crystals, while crucible (see Figure 6) is for heated drying (desiccating) of solids.

Volumetric flasks

Volumetric flasks are to be used for preparing liquids with volumes of high precision.

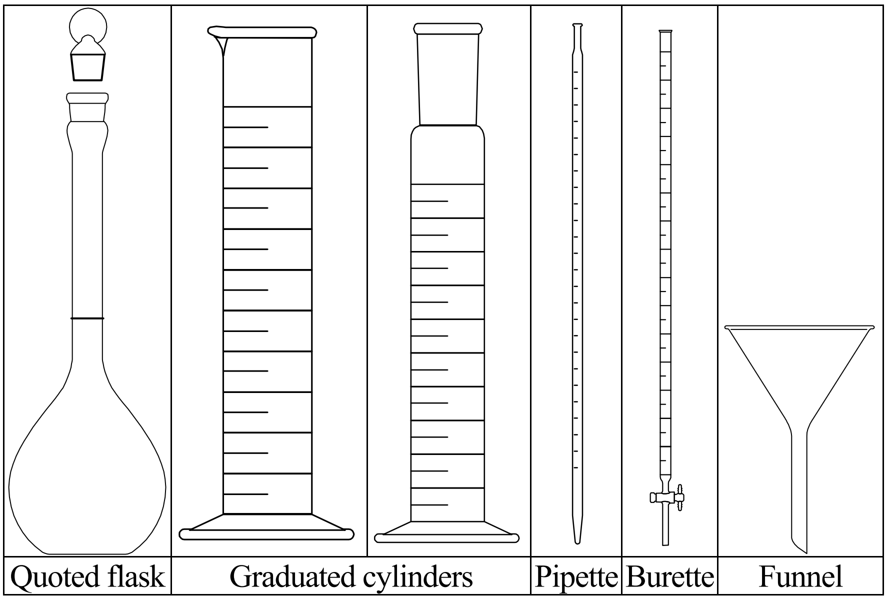


Figure 7. Quoted flask, Graduated cylinders, Burette, and Pipette

Round-bottom flasks (or quoted flasks, see Figure 7) are shaped like a tube emerging from the top of a sphere. The flasks are often long neck; sometimes they have the incision on the neck (a circumferential fill line), which precisely defines the volume of flask. Quoted flasks are used for the preparation of solutions of specified concentrations and accurate measurement of liquids volume, it have a flat bottom, and a volume from 25 mL to 3000 mL.

Graduated cylinders (with and without beak, see Figure 7) are used for measurement of volumes of liquids, being build from thick glass, and of which amount shall be given in graduated divisions. It has volumes between 5 and 2000 mL, and are labelled at the top with the working temperature (the temperature at which the volume measurements have smallest error due to dilatation effects of the glass), which is usually 20°C. Cylinders can be graduated with stopper polished without spout and are also no-tier cylinders. Anyway, with graduated cylinders measurements are approximate.

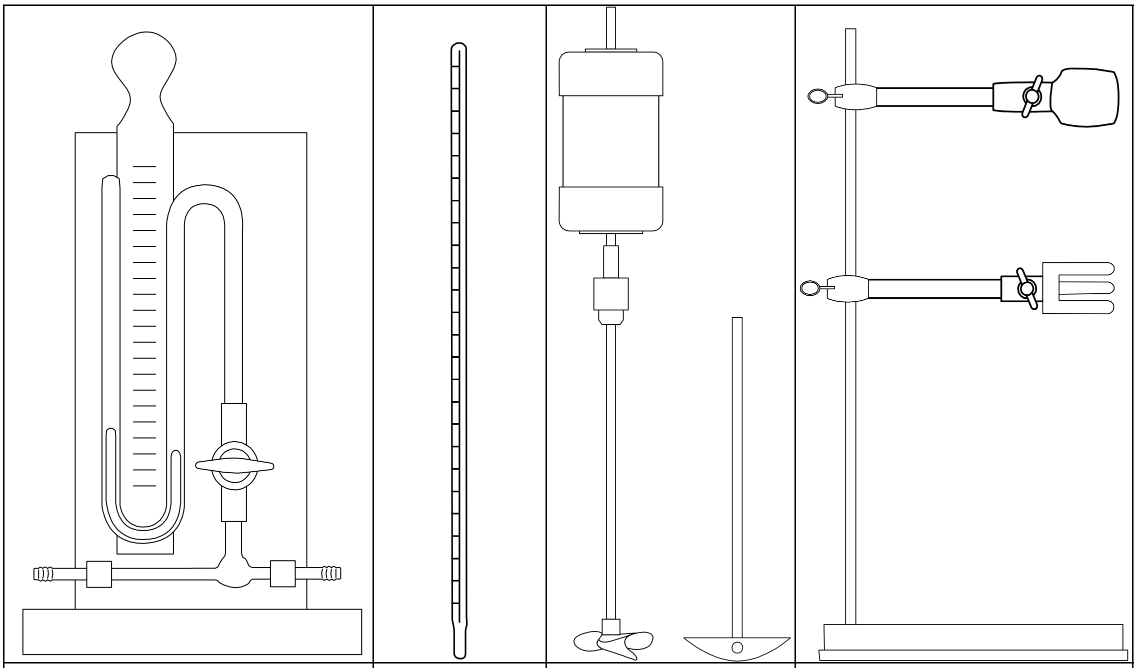
To measure the volume of a liquid with the cylinder (liquid transparent and wetting cylinder walls), this is placed on a horizontal surface and the liquid is introduced into it until the bottom of the meniscus is tangential to that mark. For coloured liquids (or mercury) meniscus reading is at the upper wetted division. Similarly are made the reading of the liquid level for other volumetric flasks, pipettes (see Figure 7) and burettes (see Figure 7).

Pipettes may have or not calibrated scale. Not-graduated ones have one or two marks and volumes between 5 and 250 mL. Graduated ones have volumes 1 mL to 25 mL. Both have usually specified the working temperature. Volatile liquids whose vapours are toxic, corrosive and toxic fluids are sucked in the pipette with a blower. Micro-pipettes are used for fast and accurate measurement of small amounts of liquid and can be landmark (used for filling) and graded, having a volume of 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 mL.

Graduated burettes are cylindrical tubes having a bottom drain tube, being used for volumetric titrations with various reagents for precise measurements of volumes. Are closed at the bottom with the valves mounted on glass or Mohr clips mounted on rubber tubes. A burette is fixed in vertical position and is filled from the top with the hopper (see Figure 7).

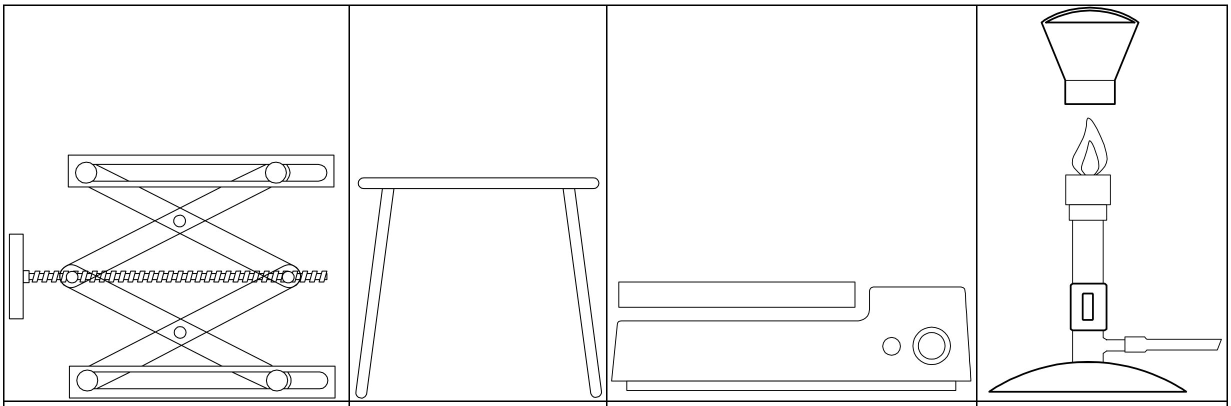
Other instrumentation in the laboratory

The other instrumentation in the laboratory usually include manometers (see Figure 8), thermometers (see Figure 8), electrical or manual stirrers (see Figure 8), glassware supports (see Figure 8) as well as lab jacks (see Figure 9), wire stands (see Figure 9), electrical heaters (see Figure 9) and Bunsen gas burners (see Figure 9).



Manometer | Thermometer | Electrical stirrer | Glassware supports

Figure 8. Manometer, Thermometer, Bunsen gas burner, and Glassware support



Lab jack | Wire stand | Electrical heater | Bunsen gas burner

Figure 9. Lab jack, Wire stand, Electrical heater, and Bunsen gas burner

Analytical balance

Introduction

Analytical balance is designed to measure small mass in the sub-milligram range. The measuring pan of an analytical balance is inside an enclosure with doors. When it used with analytical balance, the sample and the weights must be at room temperature to prevent natural convection from forming air currents inside the enclosure from causing an error in reading.

Since the weights are of order of grams, the measurements with the analytical balance are expressed in grams. Measurements with analytical balance provide four digits of precision after the dot expressing the integer part of the sample's mass in grams (example: 22.1436 g), being one of the most precise instrumentation for the measurement of masses available in the chemistry laboratory.

Operating with the analytical balance

First important point when operating with the analytical balance is to understand that the balance is so sensitive that almost never is in equilibrium and thus, please do not try to 'adjust' the balance in order to 'establish the equilibrium' by using its adjusting buttons like potentiometers of an radio!

Second important point is to understand that the balance has two operating positions, defined by the button placed at its bottom: the 'Closed' or 'Off' position, when the bottom button is rotated to maximum to the right and the 'Open' or 'On' position, when the bottom button is rotated to maximum to the left. It is very important to take aware to never use the balance with the bottom button in a position which is nor 'Open' and 'Closed' (rotated not at maximum to the right or to the left).

Third important point is to acknowledge that all the actions inside of the enclosure of the balance (manipulating weights or the sample by the right and by the left doors respectively) should be done only when the balance is in the 'Closed' position (when the bottom button is rotated to maximum to the right).

Fourth important point is to acknowledge that all operations opening and closing the balance, adding and removing the sample to the (left) plate, adding and removing weights to the (right) plate, adding and removing weights with the upper right wheels button should be done without sudden movements (in other words in 'slow motion'), because sudden movements may cause that the mechanical pieces of the ensemble of the balance to move from their equilibrium position causing disoperation of the balance.

Fifth important point is to acknowledge that the weights which are to be used with the analytical balance should be only the ones which were designed for the analytical balance, these being specially weighted to provide the desired precision of tenths of milligrams.

Balance in the OFF position can be operated to add/remove sample/weights (see Figure 1).

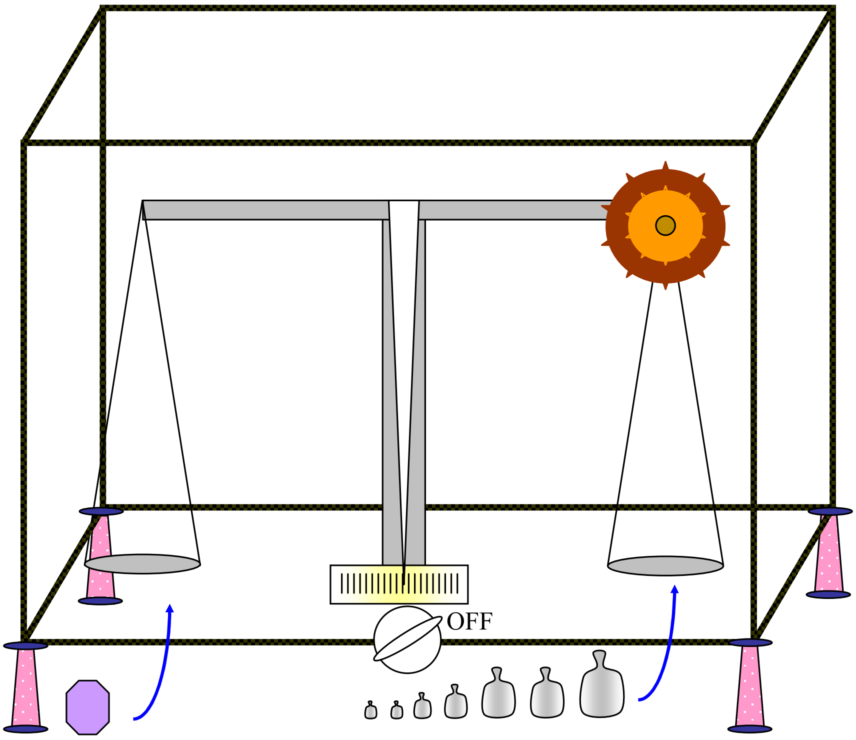


Figure 1. Analytical balance in its OFF position

Balance in the ON position cannot be operated to add/remove sample/weights (see Figure 2).

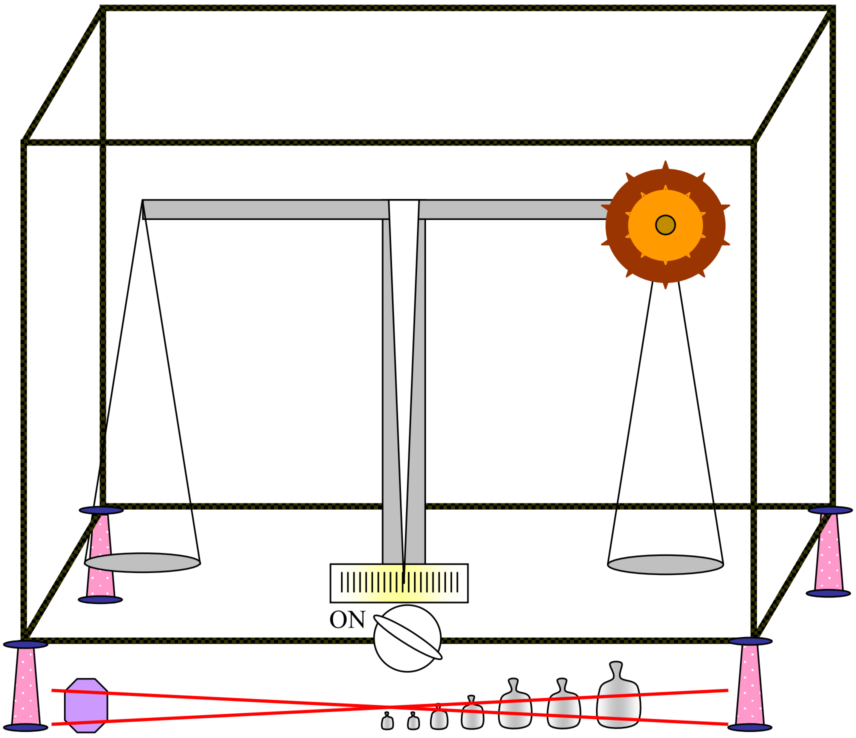


Figure 2. Analytical balance in its ON position

Using the balance

First, let us imagine what is happened when a sample is weighted. Let us suppose that we place the sample on the left plate and we place weights on the right plate. When the balance is open (rotating the bottom wheel button to the left) somebody may say that is possible to see or not the equilibrium, which is a false statement. Actually, the equilibrium is not expected to be. Is expected something else: to see the left plate (with the sample) going down and the right plate (with the weights) going up, as well as to see the central (long) indicator pointer moving to the right OR to see the left plate (with the sample) going up and the right plate (with the weights) going down, as well as to see the central (long) indicator pointer moving to the right. The meaning is simple, as is given in the next table (Table 1).

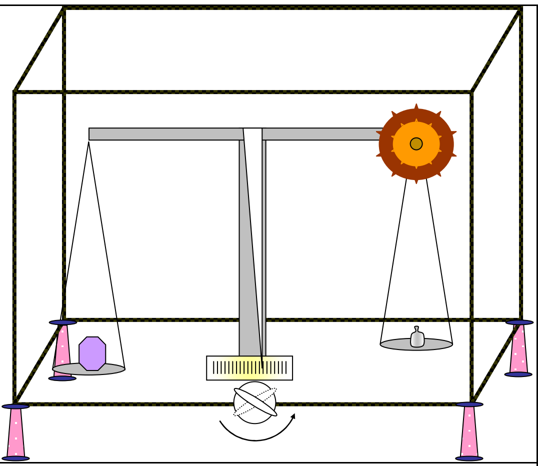
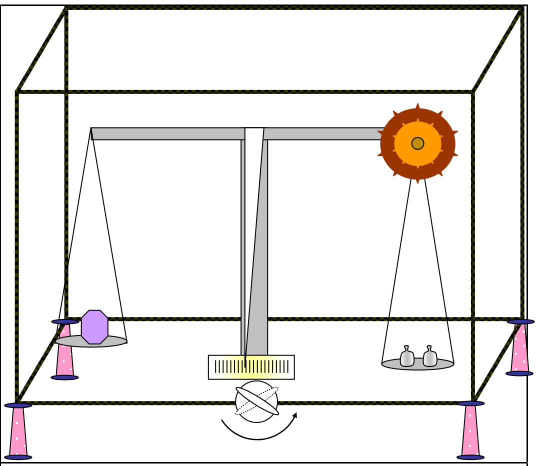
Visual		
Facts	Left plate (with the sample) goes up Right plate (with the weights) goes down Central indicator pointer moves to the left	Left plate (with the sample) goes down Right plate (with the weights) goes up Central indicator pointer moves to the right
Cause	Weights > Sample	Weights < Sample
Action to do	Remove weights	Add weights

Table 1. Behaviour when balance is opened

These visual effects (as are illustrated in the images given in Table 1) are the (only one) indications for further additions or removals of the weights.

The sample is placed on the left plate and after that a procedure which will be described in the next will be repeated three times.

Weights will be added and removed till a certain moment when the adding of a one more unit (of weight) is too more (namely with the unit we have the case 'Weights > Sample', and without the unit we have the case 'Weights < Sample').

First, this procedure of adding and removing weights is conducted with the weights available to be placed on the right plate (the weights are with the mass of 1g and some of its multipliers).

After reaching the moment when one unity (1g) is too more the unity (1g) is removed from the right plate.

Side doors of the balance will be kept from this point on (till the end of measurement) closed and the balance will be placed in the open position.

Second time the procedure of adding and removing weights is conducted with the weights available using the largest wheel from the right top corner of the balance (the weights are with the mass increasing from 0.1g to 0.9g with the step of 0.1g).

Third time the procedure of adding and removing weights is conducted with the weights available using the smallest wheel from the right top corner of the balance (the weights are with the mass increasing from 0.01g to 0.09g with the step of 0.01g).

At the end of repeating (three times) this procedure of adding and removing weights is expected that the central indicator pointer to be in range of its scale, being possible the read of the weight of the sample.

Reading the weight

Usually the individual which conduct the measurement is not the same with the one recoding the value of the mass, one reason being that the table at which the balance is placed is not intended to be used for writing (small movements on this table disturbs the balance).

The mass is recorded as follows (example: '22.1436' g):

- The weights from the right plate are added to provide the integer part of the sample's mass in grams (example: '2' + '20' = '22');
- First digit after the dot is taken from the largest wheel button (example: '1');
- Second digit the dot is taken from the largest wheel button (example: '4');
- Third and fourth digit are taken from the central indicator pointer scale which looks like a ruler of 10 cm graduated in mm in both positive and negative directions relative to 0, first (for the ruler, third for us) digit being numbered, second (for the ruler, fourth for us) digit being to be counted (example: '36', see Figure 3).

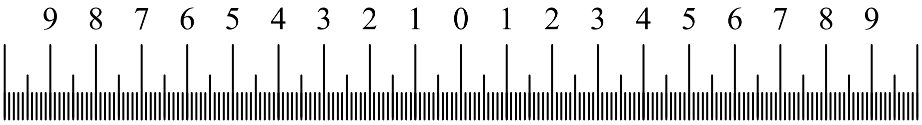


Figure 3. Central indicator pointer scale ruler

If the ruler is in its negative part, then the digits must be subtracted (example: if '36' is in the positive part, then the mass is '22.1400' + '0.0036' = '22.1436'; if '36' is in the negative part, then the mass is '22.1400' - '0.0036' = '22.1364').

After recording the measurement value, the balance is closed and after that the weights and the sample are safely removed from the balance and the upper right wheels are rotated to point zero weight.

Laboratory measurements

Introduction

Chemistry builds descriptions of nature starting from observations, passing from systematic experiments and concluding with laws. When making observations, discovering of patterns plays an important role (see also [6]).

The observing process is an activity of achieving knowledge with help of senses or instrumentation. It assumes the existing of an observer and of an observable. The observing process transfers an abstract form of the knowledge from the observable to the observer (as example as numbers or images).

Measuring comprises two serialized operations: observing and recording of the observation results. It depends on the nature of the observed object (material) or phenomena (immaterial), on the method of measurement and on the manner of recording the observation results. The concept of mathematical function is strongly connected with the concept of measurement. We can see the mathematical function definition as being the representation of our manner to record observations as measurements (see Figure 1).

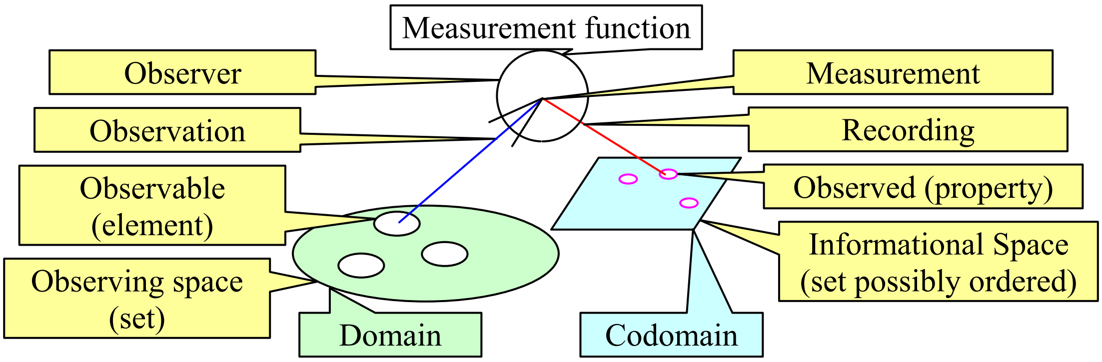


Figure 1. Collecting the experimental data is a mathematical function

As in the case of mathematical functions, when experimental measurements are conducted two properties between observed elements and their recorded properties are assured.

Namely, for all observed elements we possess records of their properties when we do measurements - having assured the serialization (SE). A measurement provides us (in a given moment of time and space) one piece of information (one record), the uniqueness (UQ) being assured too. No other known property of (mathematical) relations is not generally true for mathematical functions and nor for the measuring function. So that we can say that what information it made the measurement function is expressed by a mathematical function.

If degeneration cannot be avoided via measurement function, still can be diluted through measurement scale. It should be noticed that not all measurement scales introduces order relations (in the informational space). Natural examples are blood group and amino acids constituting the genetic code, namely is no knowledge about the existence of a natural order relation between them.

Let's take the set of two elements (C = {a, b}) and force the assumption that the order is no relevant between them. The set of subsets of C is SC = {{},{a},{b},{a,b}}. A natural order in the SC set is defined through the cardinality of the subset. Cardinality as order relation is not a strict one, because exists two subsets with same number of elements: 0 = |{}| < |{a}| = 1 = |{b}| < |{a,b}| = 2. We may ask "What kind of measurement scale cardinality defines?" - to provide a useful answer we must return to measurement and we should ask first: "Which characteristics wants to be assessed?". If the answer to the second question is the number of elements in the observed subset, then cardinality is well defined to be ***quantitative*** - *being equipped with order relation*. If differentiating between subsets of set C is the desired objective, then the cardinality of the subset is not enough. We may further construct an experiment meant for the sets with one element (for which degeneration occurs) and our measurement function to give the answer to the question "Subset contains the element *a*?" (complementary with the answer to "Subset contains the element *b*?"). This is a typical ***qualitative*** measurement - *we are looking for matches*.

Other consequence is derived wandering on account of the subsets of a set, namely the procedure of defining a measurement scale it should be at least checked from consistency point of view, or, if the scale is already defined, at least checking of its consistency in relationship with the purpose should be done.

More, even when no order relations exists, may other relations exists (such as logical complement {a} = {a,b}\{b} in the set of subsets of {a,b} set), which brings in the informational space the fact that not always results of the measurements are independent one to each other.

Going further, following table classifies by complexity (defined by the operations permitted between the recorded values) the measurement scales (see Table 1).

Scale	Type	Operations	Structure	Statistics	Examples
Binomial	Logical	"=", "!"	Boolean algebra [7]	Mode, Fisher Exact [8]	Dead/Alive Sides of a coin
(multi) Nomi(n)al	Discrete	"="	Standard set	Mode, Chi squared	ABO blood group system Living organisms classification
Ordinal	Discrete	"=", "<"	Commutative algebra	Median, Ranking	Number of atoms in molecule
Interval	Continue	"≤", "-"	Affine space (one dimensional)	Mean, StDev, Correlation, Regression, ANOVA	Temperature scale Distance scale Time scale Energy scale
Ratio	Continue	"≤", "-", "*"	Vector space (one dimensional)	GeoMean, HarMean, CV, Logarithm	Sweetness relative to sucrose pH

Table 1. Measurement scales

A measurement scale is ***nominal*** if between its values an order relation cannot be defined.

Usually nominal scale of measurement is intended to be used for qualitative measures. The binary (or ***binomial***) scale gets only two possible values (between which is no order relationship) such as: {Yes, No}, {Alive, Dead}, {Vivo, Vitro}, {Present, Absent}, {Saturated alkane, other type of compound}, {Integer, not integer}. Nominal scale with more than two possible values is called ***multinomial***. The multinomial scale of measurement has a finite number of possible values and independent of their number it exist a complementarity's relationship. Thus, for {0, A, B, AB} blood groups a value different than any three of, certain is the fourth one. A finite series of values may be considered an ***ordinal*** scale if their possible values relates through an order relationship. If we assume that "Absent"<"Present", "False"<"True", "0"<"1", "Negative"<"Nonnegative", "Nonpositive"<"Positive" then all these measurement scales are ordinal. More, an example of three-value ordinal scale is: "Negative"<"Zero"<"Positive". Other important thing about ordinal scales is that are not necessary with a finite cardinality. But are necessary to exists a order relationship defined through the "Successor" of an element function and its complement ("Predecessor"). In ***interval*** scale the distance (or difference) between possible values has a meaning. For example the difference between 30° and 40° on the temperature scale has same meaning with the difference between 70° and 80°. Range between two values is interpretable (has a physical meaning). This is the reason for which has sense to compute the mean of a variable of interval type, not applicable to ordinal scales. Such as 80° is not twice wormer than 40°, for the interval scales ratio between two values has no sense. Finally, on ***ratio*** scale, the 0 and/or 1 values have always a meaning. Assumption is that the smallest observable value is 0. It results as consequence that if two values are taken on a ratio scale, we may compute their ratio too, and also this measure possess a ratio scale of measurement.

It should be noticed that the sort of the measurement scale does not give the accuracy of the measurement too (think about accuracy thinking about the density of the possible values around the measured value).

We come back again to our subject of investigation (relating structure with the activity). The manner in which the biological property (or activity) was measured determines the manner in which we may further process and interpret the data (see *Measurement scales* again). When we measure we use a measurement scale. More, the measurement accuracy (and exactness) is of same importance as measurement value(s) itself. This is the simple reason for which commonly we express the value of a measurement together with precision of the measurement (with different approaches of expressing its value).

From the point of view of the type of measurement scale a variable (in the informational space) counting molecules from a given space is "as well as" ratio variable as a variable recording temperature of the environment in which these molecules are located, even if the result of these two operations via measurement has no comparable precision.

We should take into account that every measurement scale has own degree of organizing the information in the informational space and through this own degree of seeing the order in the observables space (see Figure 2).

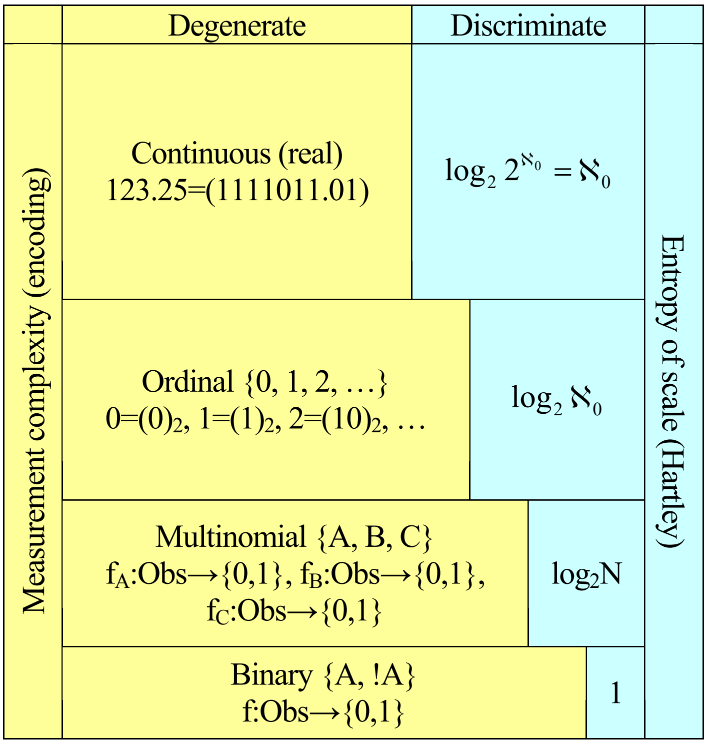


Figure 2. Degeneration vs. discrimination

The figure expresses a series of measurement scales properties. Thus, the set of binary measurement scales is placed at the basis of the triangle of measurement scales because for any other scale, we can imagine an experiment meant to give same outcome.

Indeed, the origins of the mathematical study of natural phenomena are found in the fundamental work [9] of Isaac Newton [1643-1727]. Even if first studies about binomial expressions were made by Euclid [10], the mathematical basis of the binomial distribution study was put by Jacob Bernoulli [1654-1705], of which studies of especially significance for the theory of probabilities [11] was published 8 years later after his death by his nephew, Nicolaus Bernoulli. In *Doctrinam de Permutationibus & Combinationibus* section of this fundamental work he demonstrates the Newton binomial series expansion. Later, Abraham De Moivre [1667-1754] put the basis of approximated calculus for, using the normal distribution for binomial distribution approximation [12]. Later, Johann Carl Friedrich Gauss [1777-1855] with work [13] put the basis of mathematical statistics. Abraham Wald [1902-1950, born in Cluj] do his contributions on binomial confidence intervals approximation, elaborated and published the confidence interval that carry his name now [14].

Nowadays, the most prolific researcher on confidence intervals domain is Allan Agresti, which it was named the Statistician of the Year for 2003 by American Statistical Association, and at the prize ceremony (October 14, 2003) it spoken about Binomial Confidence Intervals [15,16,17,18].

Binary observations always generate binomial distribution. A broad range of experiments are subject of binomials. Thus, law of binomial distribution are proved at heterometric bands of tetrameric enzyme in [19], the stoichiometry of the donor and acceptor chromophores implied in enzymatic ligand/receptor interactions in [20], translocation and exfoliation of type I restriction endonucleases in [21], biotinidase activity on neonatal thyroid hormone stimulator in [22], the parasite induced mortality at fish in [23], the occupancy/activity for proteins at multiple nonspecific sites containing replication in [24]. A very good essay about the frame of binomial distribution model applied to the natural phenomena is [25] and a series of its applications includes [26], [27], [28], [29] and [30].

Let us give now a close look at the binomial experiment (see *Binomial experiment*). In a binary experiment, two values may come from observation, and may be encoded as 0 and 1 in the informational space (let's say if the coin goes to the left, then is recorded 0 or it goes to the right, and then is recorded 1. In a binomial experiment, we count the number of 0's and 1's from a series of n repetitions of binary experiments (let's say from n fallen coins in our *Binomial experiment*).

If from the total time *t* of running the experiment, wind has t_1 time the direction from left to right and t_2 the direction from right to left, the expectance is to found about $100 \cdot t_1/(t_1+t_2)$% coins in the right basket and $100 \cdot t_2/(t_1+t_2)$% coins in the left basket, but the truth is that we will see a such proportion only if we will spend enough time counting the coins. Going further, we may want to estimate the wind direction ratio from counting the coins, but then what level of confidence we have for our outcome?

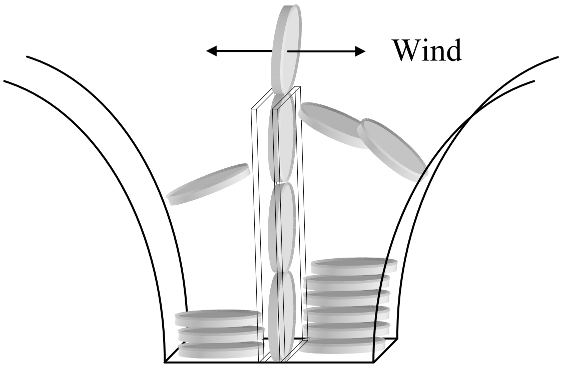


Figure 3. Binomial experiment

The previous experiment is a construction meant to estimate a ratio between two real variables (times of wind having a certain direction) in which the estimation is given from a repeated binary experiment. As longer time we will spend on counting fallen coins as better accuracy will have on estimating times ratio. This *experiment* proofs that is no difference in the quality of the measurement encoded by binary values than the measurement encoded by the real values (e.g. any real number can be encoded as a succession of 0's and 1's as in our experiment. More than that, counting the coins can be even more accurate than any other instrument if the time goes to infinity. Let's go back to the binomial experiment. The probability to see a certain number of coins in the right basket are related with wind speed ratio (or true proportion in the population) and the total number of fallen coins (see Table 2).

Coins fallen	In the right basket (probability)	In the left basket (probability)	Explanation from observation of the right basket
1	0 (p)	1 (p)	0 = 0
	1 (1-p)	0 (1-p)	1 = 1
2	0 (p^2)	2 (p^2)	0 = 0 + 0
	1 (p·(1-p)·2)	1 (p·(1-p)·2)	1 = 0 + 1 = 1 + 0
	2 ($(1-p)^2$)	0 ($(1-p)^2$)	2 = 1 + 1
…	…	…	…
n	0 (p^n)	n (p^n)	0 = 0 + 0 + … + 0
	1 ($p^{n-1}\cdot(1-p)\cdot(n)$)	n-1 ($p^{n-1}\cdot(1-p)\cdot(n)$)	1 = 1 + 0 + … + 0 = … = 0 + … + 0 + 1
	…	…	…
	k	n-k	?
	…	…	…
	n-1 ($p\cdot(1-p)^{n-1}\cdot(n)$)	1 ($p\cdot(1-p)^{n-1}\cdot(n)$)	n-1 = 0 + 1 + … + 1 = … = 1 + … + 1 + 0
	n ($(1-p)^n$)	0 ($(1-p)^n$)	n = 1 + 1 + … + 1

?: The probability of falling k from n comes from the Newton's binomial expansion (and may be verified by induction):

$$\left(p+(1-p)\right)^n=\sum_{k=0}^{n}\frac{n!}{k!(n-k)!}p^k(1-p)^{n-k}$$

Table 2. Binomial distribution

According to [31] in general if *p* is a population parameter, T_1 a sufficient statistic in estimating *p*, and T_2 is any other statistic, the sampling distribution of simultaneous values of T_1 and T_2 must be such that for any given value of T_1, the distribution of T_2 does not involve *p* (if $f(p,T_1,T_2)dT_1dT_2$ - probability that T_1 and T_2 to fall in ranges dT_1 and dT_2 - it separates as follows: $f(p,T_1,T_2) = f_1(p,T_1)\cdot f_2(T_1,T_2)$.

The probability of drawing in order any particular sample $x_1, x_2, \ldots, x_n$ (of 0's and 1's) is:

$$p^{x_1}(1-p)^{1-x_1}\cdot\ldots\cdot p^{x_n}(1-p)^{1-x_n}=p^{\Sigma x_i}(1-p)^{n-\Sigma x_i}=\frac{n!}{(\Sigma x_i)!(n-\Sigma x_i)!}p^{\Sigma x_i}(1-p)^{n-\Sigma x_i}\cdot\frac{(\Sigma x_i)!(n-\Sigma x_i)!}{n!}$$

Above the quantity was divided in two factors of which the first represent the probability that the actual total Σx_i should have been scored, and the second the probability, given this total, that the partition of it among the *n* observations should be actually observed. In the latter factor, *p*, the parameter sought, does not appear. Now when the mean Σx_i is known, any further information which the sample has to give depends on the observed partition ($\Sigma x_i/(n-\Sigma x_i)$), but the probability of any particular distribution is wholly independent of the value of *p*.

The parameter *p* can be estimated from the mean of the observed sample by using the Maximum Likelihood Estimation (MLE) method [32]:

$$\mathrm{MLE}=\ln\left(\frac{n!}{(\Sigma x_i)!(n-\Sigma x_i)!}p^{\Sigma x_i}(1-p)^{n-\Sigma x_i}\right)=\max.\ \text{then}\ \frac{\partial \mathrm{MLE}}{\partial p}=\frac{\partial \mathrm{MLE}}{\partial n}=0$$

The parameters *n* and *p* are independent, and then from ∂MLE/∂p = 0 it results:

$$\frac{\partial}{\partial p}\ln\left(\frac{n!}{(\Sigma x_i)!(n-\Sigma x_i)!}\right)+\frac{\partial}{\partial p}\ln\left(p^{\Sigma x_i}\right)+\frac{\partial}{\partial p}\ln\left((1-p)^{n-\Sigma x_i}\right)=0$$

This previous equation gives a relationship between estimators under assumption of the maximum likelihood:

$$\frac{\Sigma x_i}{p}-\frac{n-\Sigma x_i}{1-p}=0\text{, from which }\hat{p}\cdot\hat{n}=\Sigma x_i$$

Solution of the second derivative (∂MLE/∂n = 0) has no analytical close form and can be computed only numerically [33]. Thus, if we assume that we draw always *n* objects, then $T_1 = \Sigma x_i$ is a sufficient statistics. More, if we obtain an estimate of $p, \hat{p}$, from $\hat{p}\cdot n=\Sigma x_i$, then (as long is the solution of MLE) then:

$$\operatorname{var}(\hat{p})=\left(-\left(\frac{\partial^2 \mathrm{MLE}}{\partial p^2}\right)\right)^{-1}=\left(\frac{\Sigma x_i}{p^2}+\frac{n-\Sigma x_i}{(1-p)^2}\right)^{-1}=_{\hat{p}\cdot n=\Sigma x_i}\left(\frac{\hat{p}\cdot n}{p^2}+\frac{n-\hat{p}\cdot n}{(1-p)^2}\right)^{-1}=_{p=\hat{p}}\frac{p(1-p)}{n}$$

Confidence for a binomial proportion is relatively simple to be expressed as long as we enumerate entire probability space of the binomial distribution.

A variable (Y) confined to the whole domain of values (from 0 to n) is binomial distributed if the probability of its taking any particular value *j* is $P_B(Y = j)$. When we already conducted a previous experiment in which we seen *i* objects on the right from *m* objects in total, then we can use *i/m* as an estimate for *p* and the probability of *Y* taking *j* values on the right become $P_B(Y = j, n, i/m)$:

$$P_B(Y=j)=\frac{n!}{j!(n-j)!}p^j(1-p)^{n-j},\ P_B(Y=j,n,i/m)=\frac{n!}{j!(n-j)!}\left(\frac{i}{m}\right)^j\left(1-\frac{i}{m}\right)^{n-j}$$

In order to collect the probabilities given by the previous relation and to express a 95% (or other threshold) confidence interval we must solve a combinatorial problem since $P_B(j)$ function is not monotone nor continuous.

It is a fact that we cannot express a mathematical formula indicating how many numbers from left and how many from right should be excluded in general when we express a confidence interval from a binomial experiment (for more details see [34]). For this reason usually expressed confidence intervals uses approximating formulas. Following table lists the most known of it.

Group	Name	Method	Acronym*	Refs
Normality approximation	Wald	Classic	Wald_N	[14],[35], [36], [37]
		Continuity corrected	Wald_C	[38]
	Agresti-Coull	Classic	A_C_N	[15]
		Continuity corrected	A_C_C	[38]
		Continuity corrected	A_C_D	-**
	Wilson	Classic	Wilson_N	[39]
		Continuity corrected	Wilson_C	[36]

Group	Name	Method	Acronym*	Refs
Harmonic approximation	ArcSine	Classic	ArcS_N	[40]
		Continuity corrected	ArcS_C	[38]
		Continuity corrected	ArcS_D	[38]
		Continuity corrected	ArcS_E	-
Log-normality approximation	Logit	Classic	Logit_N	[41]
		Continuity corrected	Logit_C	[42]
Binomial approximation	Bayes (Fisher)	Classic	BetaC11	[43]
	Clopper-Pearson	Classic	BetaC01	[44], [45]
	Jeffreys	Classic	BetaCJ0	[46]
	BetaC00	Continuity corrected	BetaC00	-
	BetaC10	Continuity corrected	BetaC10	-
	BetaCJ1	Continuity corrected	BetaCJ1	-
	BetaCJ2	Continuity corrected	BetaCJ2	-
	BetaCJA	Continuity corrected	BetaCJA	-
Obtained from optimization	Blyth-Still-Cassella	Probabilistic optimization	B_S_C	[47], [48]
	OptiBin	Numerical optimization	OptiBin	[49]
	ComB	Combinatorial enumeration	ComB	[50], [51]
* As at: http://l.academicdirect.org/Statistics/confidence_intervals; see also Table 1 p. 42 in [52]				

Table 3. Binomial and Binomial-like confidence intervals

A more complex problem occurs when expressions containing proportions requires confidence intervals. This is the common case when ratios or differences of proportions express a relative or absolute measure of comparison between two populations, or two treatments on populations. This sort of expressions is often used in medical and biological studies (see [52] and [53]).

The general shape of a study involving two binomial proportions is given by a 2X2 contingency table (see *2X2 contingency*).

2X2 contingency

Experiment 1\2	Left	Right
Up	a	b
Down	c	d

Expressions involving two binomials

Function	f3	f4	f5	f6	f7	f8
Expression	$\frac{X(n-Y)}{Y(m-X)}$	$\frac{Y}{n}-\frac{X}{m}$	$\left\lvert\frac{Y}{n}-\frac{X}{m}\right\rvert$	$1/\left\lvert\frac{Y}{n}-\frac{X}{m}\right\rvert$	$\frac{Xn}{Ym}$	$\left\lvert 1-\frac{Xn}{Ym}\right\rvert$

Table 4. Calculations on 2X2 contingency

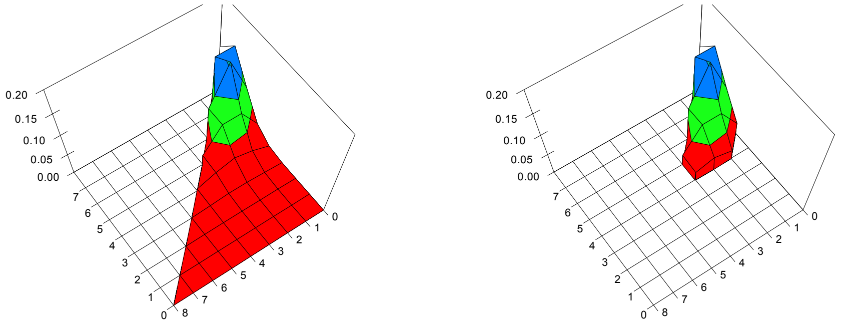
Depending on the type of the experiment, a list of six binomial expressions involving two binomial variables may comprise the currently reported in the literature [52] (see *Expressions involving two binomials*) - where the place of X and Y in the contingency table may vary (for example one arrangement is when X = a, m = a+b, Y = c, n = c+d and other one is when X = a, m = a+c, Y = b, n = b+d).

If the observations are split into the informational space in more than two categories then knowing as a fact that we observe *n* objects which falls in *k* classes with the probabilities $p_1, p_2, \ldots, p_k$ $(1 = p_1 + p_2 + \ldots + p_k)$ then the probability $P_M(x_1, \ldots, x_n; n; p_1, \ldots, p_k)$ to observe a certain distribution of the objects $(n = x_1 + x_2 + \ldots + x_k)$ in the classes $(1, \ldots, k)$ is:

$$P_M(x_i;n;p_i) = n!\prod_{j=1}^{k} p_j^{x_j} \Big/ x_j!$$

We have many multinomial distributions when we discuss about the distribution of living organisms in a certain area, for example distribution of bacteria species belonging on a class of bacteria in a Petri plate after treatment with an antibiotic. Also for these cases we want to express with a certain level of confidence, the effect of the treatment, for example.

Our knowledge about expressing confidence for expressions containing binomial variables can be extent to cover trinomial (see *Trinomial(6A,1B,1C) - distribution and 95% coverage confidence interval*) or multinomial variables as well [54].



Depicted: X (for A) - in depth axis, Y (for B) - left-to-right axis, $P_3(X,Y,Z)$ - vertical axis

Figure 4. Trinomial(6A,1B,1C) - distribution and 95% coverage confidence interval

Thus, any measurement on any three categories nominal scale may be seen as a series of two binary measurements (f_A="*if A then 0 else 1*"; f_B="*if B then 1 else 0*") and this series of two measurements is equivalent with a measurement on the three categories nominal scale meant to classify in *A*, *B*, and *C* categories. Going further, {A, B, C} will be equivalent encoded in the informational space by {10, 01, 00}. Similarly {0, 1, 2, …} can (and often is) equivalent encoded in the informational space as (infinite) arrays (shown here in reverse order as we see the numbers in computer): 0→(000...), 1→(100...), 2→(010...), etc. For real values from [0,1) again providing the (infinite) series $\Sigma_{i\geq1}a_i\cdot2^{-i}$, where $a_i\in\{0,1\}$ we gain a unique encoding for every number from [0,1) as a (infinite) series of binary values starting with 0: $0.a_1a_2\ldots$; even further, the f(x)=1/(x-1) give us a unique correspondence between [0,1) and [0,∞). This extent can be pushed forward to encode the sign too, and thus the existence of the binary scale is enough to construct any real representation (and the computers do this).

Regarding the computation of the discriminating power of one scale relative to another, we take this value from the total number of the distinct values encoded in the informational space, and Hartley's entropy [55] sorts from this point of view of discriminating power the measurement scales.

Sampling

All procedures of quantitative analysis includes some common laboratory operations: taking of the samples, drying, weighting and solvation [56]. Solvation is the only operation which is not always necessary because exists some instrumental methods in which measurement is possible directly on the sample [57]. Any experienced analyst performs these operations by giving them special attention, since it is known that adequate preparation for measurement is as important as the measurement itself. A sample must be representative for all components taking into account the extent to which these components are included in the material to be analyzed. If the material is homogeneous, sampling is not a problem. For heterogeneous materials special precautions are required to obtain a representative sample. A sample sized laboratory can choose by chance or you can select a plan developed statistically, which theoretically gives each component in the sample an equal chance of being detected and analyzed.

Sampling from gaseous phase

There are 3 basic methods for collecting the gases. These are: the expansion of a container that can then be discharged, washing and replacement of a liquid.

In all cases, you must know the volumes collecting vessels, temperature and pressure. Typically, the collection vessels are made of glass and equipped with an inlet and an outlet which can be opened and closed suitably. To eliminate contamination of samples, wash the outside of the container with the gas to be sampled. Concept sampling device must allow this process to run smoothly. Air is a complex mixture of different gases. Its actual composition is dependent on the environment and on where the sample is taken. Currently, due to pollution, more efforts are directed to study and monitor the air quality. The presence of air can cause various compounds that give specific colour reactions, the amount of anions in the air (by reaction with a basic solution), or the amount of cations in the air (the reaction with an acid solution).

In order to collect an air sample a simple collector is depicted below which also measure the sample volume of air. In order to determine the concentration of anions in the air a possibility is by titrating with a suitable base (NaOH), as the Figure 5 provides a schematic of an experimental installation.

Working procedure can be imagined as follows:

÷ Measure the ambient temperature thermometer T;

÷ Measure the ambient pressure p with the barometer;

÷ Add the solution to capture the volume V of the air: 20 ml. solution of $CaCl_2$ 0.1M and 20 ml solution of NaOH 0.1M;

÷ Fill with distilled water above the lower tube;

÷ Add a indicator for the presence of the pH = 7 (for instance bromothymol blue);

÷ Measure the diameter of the air inlet tube in the vicinity of the pressure gauge; let be d;

- Start the water pump so that the flow is constant, visible and small;
- Start the timer and measure the time until the color change is observed in the capture solution; let be t.

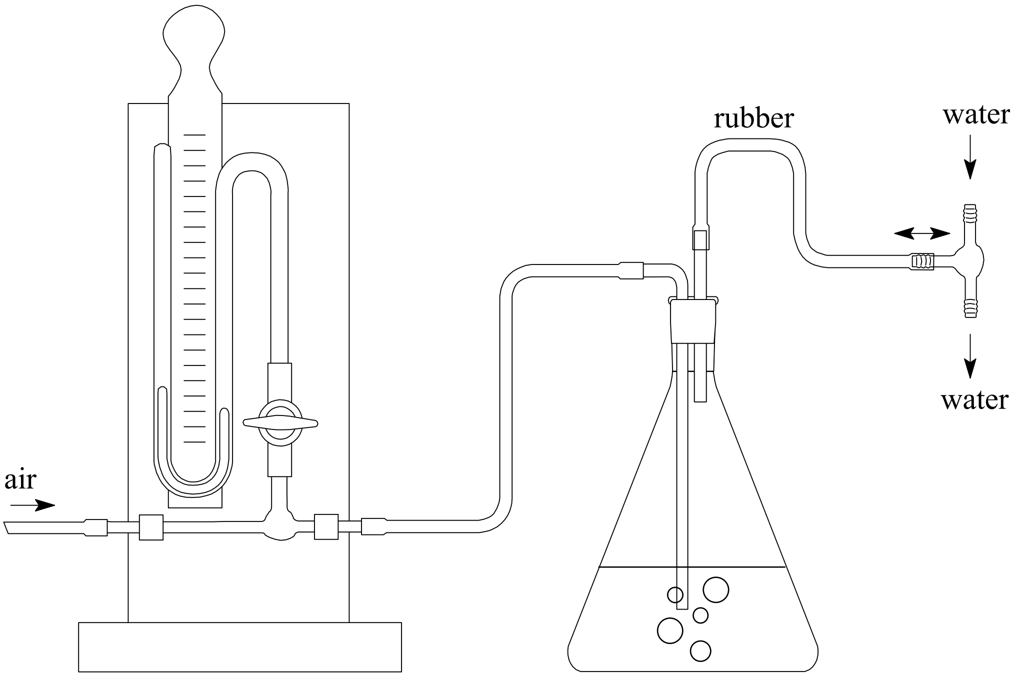


Figure 5. Capturing samples of air in solution

Equalizing the pressure of the air stream dynamic pressure due to the elevation of the column of fluid in the pressure gauge, the resulting air flow velocity through the tube:
$v^2 = 2 \cdot g \cdot h \cdot \rho_l / \rho_{air}$, where g is the gravitational acceleration ($g = 9.8065\ ms^{-2}$), h is the difference between the heights of the liquid columns in the manometer (m), ρ_l is the density of the liquid in the manometer (for water $\rho_l = 1000\ kg/m^3$), ρ_{aer} is the density of the iar in the conditions of temperature and pressure from the laboratory, from: $\rho_{air} = p \cdot M/(R \cdot T)$, where p the atmospheric pressure (in N/m^2), M the molecular mass of the air ($M = 28.9 \cdot 10^{-3}$ kg/mol can be used), R is the gas constant ($R = 8.31$ J/mol·K), T is the absolute temperature (in K). The volume of the air consuming the entire quantity of NaOH is given by the relation $V = v \cdot t \cdot S$, where v is the speed of the air flow, t is the neutralization time (s) and S (m^2) is the section of the tube ($S = \pi \cdot d^2/4$). Quantity of anions comes from the equivalence with the quantity of NaOH neutralized: n_{NaOH}, when the concentration of the anions in air is: $c_{air} = n_{NaOH}/V$.

Sampling from liquid phase

Taking samples of pure or homogeneous liquid is straightforward and usually you can use any device that does not destroy the purity or homogeneity. Sampling of heterogeneous liquid mixtures poses some difficult problems. The method used was selected based on the mixture to be analyzed, that is a suspension, an emulsion, a mixture of immiscible liquid phases, or a liquid containing solid residues. When the liquid mixture is unstable (such as an emulsion) or if contains volatile components or if contains dissolved gases then additional difficulties arises. In general, aliquots are taken at random from different depths and in all places in the liquid sample. They can be analyzed separately or can be combined to give a sample composition, the static, representative of the original sample. Mixtures of immiscible liquids are quite common in the art. The best known are mixtures of gasoline and oil + water + water. Accidental oil spills are very unpleasant events ecosystems. For these mixtures phase separation and then measuring the mixing ratio quantitative analysis of the separated fractions are common methods in instrumental analysis of liquids. In addition to miscibility (in percent by weight usually) a mixture of liquid is characterized by the distribution coefficient, which is defined for distribution of a compound present in the mixture of the two phases, expressed as a weight ratio.

From a mixture of non-miscible liquids is possible to extract a solved component (Figure 6).

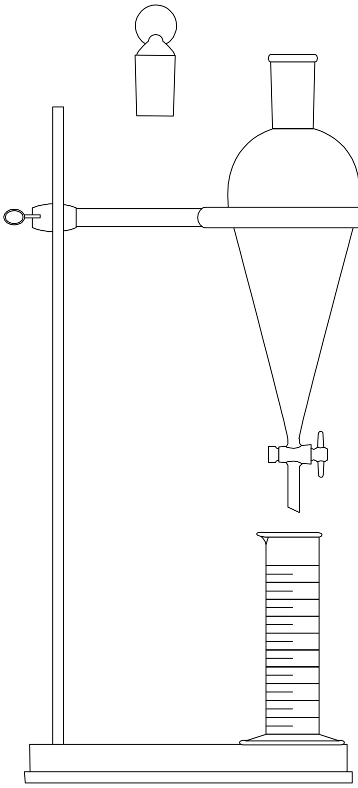


Figure 6. Extraction from a mixture of two non-miscible liquids

For two-component systems the separation of the two liquid phases is not total in general, especially when one of the components is water and the other a liquid partially miscible with water. To design an extraction mixture should be considered after evaluation of their miscibility in water.

Sampling from solid phase

Analysis of the solids can be made directly in the solid phase by means of emission or absorption of radiation in the arc or flame (see [58]) or by moving the solid material in the form of a solution by dissolution with or without changing the oxidation state of the constituent elements, following the determination of the composition to be then make liquid phase by specific methods.

If the solid is homogeneous, any part can be selected as representative. For a heterogeneous solid a plan should be prepared to reach all sections of solid statistical sampling. Sampling can be done manually or mechanically, when the material to be analyzed has a large table (see Figure 7).

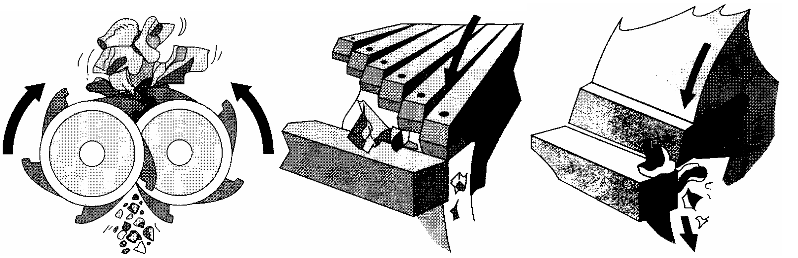


Figure 7. Devices for reducing sample size: crusher, transversal and parallel cutters

It is not always possible to obtain statistically, a representative sample. For example, it is obviously a difficult task to determine the surface composition of. Starting with a limited amount of rock and dust sampling has been based in part on the size of the particles and partly on their physical condition. Particle size is an important parameter in the sampling of a solid, because the composition of particles of different sizes can vary. In general, higher conversion of a sample in a sample of suitable size for analysis requires, first, the reduction of the sample to a uniform particle size and second, the reduction in mass of the sample. A uniform particle size is obtained by passing the sample through crushers, pulverizers, mills or mortars. It can also be used for screening granular or metal filing. Whatever the method chosen, it is necessary to ensure that these operations will not contaminate the sample.

Drying

After obtaining the corresponding sample, further analysis will be decided if will be conducted with whether the sample as such or after it has been dried. Most samples contain varying amounts of water due to the fact that the sample is hygroscopic or water is absorbed at the surface. The drying operation is typically by heating in an oven, a muffle furnace or combustion Bunsen or Meeker lamps.

Since heat is used for drying, it is possible that the sample drying her attempt to decompose or lose volatiles. Both cases must be considered in making a correct analysis. After the sample was dried, will be typically weight. To do this, use the scales. Balances are mass measuring instruments, but there are several types: technical balance (with precision of grams used for weights of substances whose mass exceeding 1 kg), pharmaceutical balance (precision of 1 to 10 mg used for weights of substances whose mass exceeds 100g), analytical balance (precision 0.1 mg used for weighing substances whose weight is below 100g), electronic scales (table-recording changes over time) [1].

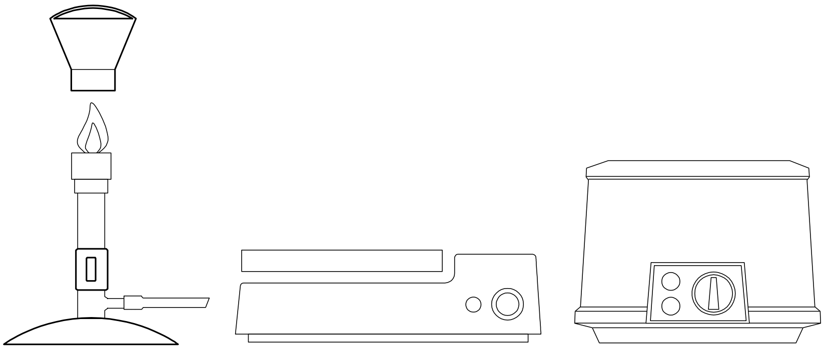


Figure 8. Devices for drying the samples

Dissolving

After weighing the sample, the next step may be dissolving. If the sample is soluble in water, there is no problem of the dissolution, though sometimes slow sample may hydrolyze in water to form insoluble compounds. Organic materials are commonly dissolved in organic solvents or in mixtures of organic solvents and water. There are a variety of chemical processes and tools that require a specific solvent composition. In other cases it not necessary the step of dissolution. Thus, the sample is excited in the arc or spark and then analyzes the resulting radiant energy can be used directly in a liquid or solid sample. If required to be considered organic part of the mixture of sample taken, then you must use specific organic solvents and organic chemistry technologies. For inorganic samples, the most frequent in the industry, the sample is dissolved in an acid or a flux melts. When using acids, it is important to know the chemical properties of the sample, if necessary oxidizing or non-oxidizing acid, if the process applied must comply with restrictions on the type of anion in solution, and if after dissolution should be deleted or not excess the acid.

Specific situations: H_2SO_4 should not be used for samples containing Ba ($BaSO_4$ is a white precipitate which is insoluble); HCl should not be used for samples with Ag or Ag salts (AgCl is a white precipitate which is insoluble). The selection of the particular acid to be used for the dissolution is carried out on the basis of their chemical properties, they are oxidising or non-oxidising. Non-oxidising acids used are HCl, diluted H_2SO_4, and diluted $HClO_4$. Oxidizing acids are: HNO_3, H_2SO_4 and hot concentrated $HClO_4$. The dissolution of the metal by means of non-oxidising acids is based on the ability of metals to replace hydrogen. In this case, you must take into account the chemical activity series of metals

Li, Ca, K, Ba, Na, Mg, Al, Zn, Fe, Cd, Co, Ni, Sn, Pb, H, Cu, Ag, Hg, Au

The stronger oxidizing conditions are obtained with the use of hot and concentrated $HClO_4$, usual dissolving all metals. Often advantages are gained from the use of combination of acids. The most familiar is aqua regia (1:3 of HNO3:HCl) from which HNO_3 is an oxidant and HCl have complexing properties and provide strong acidity. Note that the solubility of many metal ions is maintained only in the presence of complexing agents. Hydrogen fluoride (HF), although a weak acid and non-oxidizing, provides rapid decomposition of silicate samples with SIF_4 obtaining. It have a higher complexing action than hydrochloric acid (HCl). HNO_3+$HClO_4$ mixture has a much more vigorous action to dissolve, but require more careful handling because it can cause explosions.

Fluxing is more effective than treatment with acid for two reasons. First, due to the higher temperature necessary for melting (from 300 °C to 1000 °C) is the reaction processes to be carried out more easily. The second advantage is that if fluxes in contact with the sample there is a greater amount of reactive, making the reaction is faster and more shifted towards the formation of products.

Sampling distribution and distribution analysis

Systematic repeated measurements of a certain characteristic from a population lead to the concept of distribution from sampling. Let be a statistic in a population subject to measurement. The sampling distribution is the distribution of that statistic, considered as a random variable, when derived from a random sample of fixed size n. It may be considered as the distribution of the statistic for all possible samples from the same population of a given size. The sampling distribution depends on the underlying distribution of the population, the statistic being considered, the sampling procedure employed, and the sample size used. There is often considerable interest in whether the sampling distribution can be approximated by an asymptotic distribution, which corresponds to the limiting case as $n \to \infty$.

There are a series of known (theoretical) distributions and when repeated sampling is involved, the expectance is that data to fit to a known distribution. Usually this stage supposes to assess the fit of the data to one or more alternatives and involves using of a series of statistics measuring the agreement (see [59], [60], [61] and [62] for further details).

When exists a doubt about the celerity with which the data was collected, a useful test is the Benford test [63].

When measurements are more likely opinions recorded on ordinal scales (see for instance [64] and [65]) then testing for a binomial proportion may require optimization of the distribution parameters, as were conducted in [66] and [67].

When contingencies are behind the observation, then using of the Chi-Squared statistic (see [68]) is a good alternative, as is exemplified in [69], and in other cases design of the experiment (see [70], [71], [72] and [73]) is the preliminary step (the factor analysis may be the second one, as exemplified in [74] and [75]) through the characterization of the population, as is exemplified in [76], [77], [78], [79], [80] and [81].

In some cases, the phenomena lead to the distribution (see [82], [83] for details). In other cases, recording of the observed distribution may be enough to characterize the phenomena (as is exemplified in [84]) while in other cases may have as outcome a statistic (see [85]).

The most convenient case is when enough data for obtaining the distribution of the population are available (see typical cases in: [86], [87], [88], [89], [90], [91]) but also from incomplete data some information may be successfully extracted (see [92], [93], [94] and [95]).

Rarefaction method may help to reconstruct the sampling distribution (see [96] for details) and smoothing may help to indicate the general tendency (see [97], [98], [99], and [100]).

Association and regression analysis

The expected result when an association between paired observations is under investigation is the linearity (see [101], [102], [103], [104] and [105]; see as examples of linear regression analysis: [106], [107], [108], [109], [110], [111], [112], [113], [114], [115], [116], [117], [118], [119], [120], [121], [122], [123], [124], [125], [126], [127], [128], [129], and [130]), but other models may occurs too (see [131], [132], [133], [134], [135], [136] and [137]).

A difficult task is to assess the quality of the regression model (see [138], [139], [140], [141], [142], [143], [144], [145], [146], [147] and [148] for details).

Study of the diffusion in gaseous state and molecular speeds

Introduction

Were established following inequalities (see Ex.23 in [5]; see also [149]), in which the energy at mode is smaller than the energy of the molecules with the mode speed, which is smaller than the energy of the molecules with average speed, which is smaller than the energy of the molecules with the speed equal with average of squared speed:

$$\hat{\varepsilon} = \frac{J-2}{2} \cdot k_B T \le \frac{m\hat{s}^2}{2} = \frac{J-1}{2} \cdot k_B T \le \frac{m\bar{s}^2}{2} = \left(\Gamma\left(\frac{J+1}{2}\right) \Big/ \Gamma\left(\frac{J}{2}\right)\right)^2 \cdot k_B T \le \bar{\varepsilon} = \frac{J}{2} \cdot k_B T$$

Expressing the relationships on R·T ($R = k_B \cdot N_A$; $m \cdot N_A = M$):

$$RT = \frac{Ms_{\hat{\varepsilon}}^{\ 2}}{J-2} = \frac{Ms_{\hat{s}}^{\ 2}}{J-1} = \frac{Ms_{\bar{s}}^{\ 2}}{2\left(\Gamma((J+1)/2)/\Gamma(J/2)\right)^2} = \frac{Ms_{\bar{\varepsilon}}^{\ 2}}{J}$$

For two gases at the same temperature the $k_B \cdot T$ term is the same, allowing the obtaining of a relationship between the masses and the speeds. This law can be easily verified experimentally with a simple experiment of diffusion in gaseous state. Are phrased thus the hypothesis that the diffusion speed is proportional with the speed of the molecules. For the speed of the molecules we have, as was shown above, more than one statistic: real speeds (when the number of the energy components J, is always 3) and virtual speeds (when the number of the energy components depends on the structure of the molecules).

Thus, are opened the problem to identify which is the number of the energy components (labeled with *J*) which are used by the molecules in the diffusion process, and here the effect can be with the models expressed from virtual (labeled as *s*), or real (labeled as *v*) speeds, which of the statistics, namely the mean (labeled with an over-bar) or the mode (labeled with an hat) as well as which of the physical quantity: speed (labeled with s) or energy (labeled with ε, $\varepsilon \sim s^2$) correspond to the observable (formation of the NH_4Cl ring in the experiment which will be conducted).

Purpose

Establishing by experimental path the diffusion speeds, and on this way, of the model linking the diffusion speeds with the molecular speeds (seen as molecular statistics) derived from molecular kinetic theory, leading to the obtaining of the diffusion coefficients.

Material and method

It will be studied the reaction in gaseous state between ammonia and hydrochloric acid. Both these substances are solved in water, and thus a series chemical reactions can be written, as are given in the next table (see Table 1).

No	Equilibrium chemical reaction
R1	$HCl + H_2O \leftrightarrow Cl^- + H_3O^+$
R2	$NH_3 + H_2O \leftrightarrow NH_4^+ + HO^-$
R3	$NH_3 + HCl \leftrightarrow NH_4Cl$
R4	$NH_4^+ + Cl^- \leftrightarrow NH_4Cl$

Table 1. Models for reaction in gaseous state for the reaction producing ammonium chloride

Supposing that at environmental temperature the number of the energy components can be approximated with the number of degrees of freedom, starting from structure of the compounds can be calculated the squares of the virtual (s) and real (v) speeds, for each reactant candidate leading to formation of ammonium chloride intended to be observed in the experiment (the reactants involved in the reactions R3 and R4). The calculation are given in the next table (M(H) = 1.008; M(N) = 14.007; M(Cl) = 35.45 g/mol):

$$s_{\hat{\varepsilon}}^2 = \frac{J-2}{M}\cdot RT;\ s_{\hat{s}}^2 = \frac{J-1}{M}\cdot RT;\ s_{\bar{s}}^2 = \frac{2}{M}\left(\frac{\Gamma((J+1)/2)}{\Gamma(J/2)}\right)^2\cdot RT;\ s_{\bar{\varepsilon}}^2 = \frac{J}{M}\cdot RT;\ \frac{v^2}{3} = \frac{s^2}{J}$$

By applying the above given formulas to the species (NH_3, HCl, NH_4^+, Cl^-) and to their corresponding degrees of freedom (6, 5, 6, 3), following calculation allows expressing of the constant terms multiplying R·T (where T is the temperature and R is the ideal gases constant):

↓										
Specie	M	df= J	$\frac{s_{\hat{\varepsilon}}^2}{RT}=$	$\frac{s_{\hat{s}}^2}{RT}=$	$\frac{s_{\bar{s}}^2}{RT}=$	$\frac{s_{\bar{\varepsilon}}^2}{RT}=$	$\frac{v_{\hat{\varepsilon}}^2}{RT}=$	$\frac{v_{\hat{s}}^2}{RT}=$	$\frac{v_{\bar{s}}^2}{RT}=$	$\frac{v_{\bar{\varepsilon}}^2}{RT}=$
NH_3	17.031	6	0.2349	0.2936	0.3243	0.3523	0.1174	0.1468	0.1621	0.1761
HCl	35.45	5	0.0823	0.1097	0.1242	0.1371	0.0494	0.0658	0.0745	0.0823
NH_4^+	18.039	6	0.2217	0.2772	0.3061	0.3326	0.1109	0.1386	0.1531	0.1663
Cl^-	36.458	3	0.0282	0.0564	0.0718	0.0846	0.0282	0.0564	0.0718	0.0846

Applying square root, more convenient expressions are obtained, allowing the direct extraction of the speed formula, as a coefficient multiplying $\sqrt{RT}$ term:

Specie	M	df= J	$\frac{s_{\hat{\varepsilon}}}{\sqrt{RT}}=$	$\frac{s_{\hat{s}}}{\sqrt{RT}}=$	$\frac{s_{\bar{s}}}{\sqrt{RT}}=$	$\frac{s_{\bar{\varepsilon}}}{\sqrt{RT}}=$	$\frac{v_{\hat{\varepsilon}}}{\sqrt{RT}}=$	$\frac{v_{\hat{s}}}{\sqrt{RT}}=$	$\frac{v_{\bar{s}}}{\sqrt{RT}}=$	$\frac{v_{\bar{\varepsilon}}}{\sqrt{RT}}=$
NH_3	17.031	6	0.4847	0.5418	0.5695	0.5935	0.3426	0.3831	0.4026	0.4196
HCl	35.45	5	0.2869	0.3312	0.3524	0.3703	0.2223	0.2565	0.2729	0.2869
NH_4^+	18.039	6	0.4709	0.5265	0.5533	0.5767	0.3330	0.3723	0.3913	0.4078
Cl^-	36.458	3	0.1679	0.2375	0.2680	0.2909	0.1679	0.2375	0.2680	0.2909
$R = 8.134\ J\cdot mol^{-1}\cdot K^{-1}$ (ideal gases constant)										

Table 2. Summary of theoretical models

If the speeds given above are divided, a series of speed ratios are obtained. Thus is possible to compare these ratios with the ratio obtained from the experiment for the diffusion speeds. The outcome of this comparison is the decision of which of the molecular speeds are used by the molecules for diffusion, and respectively which chemical species diffuses, the neutral or the ionic ones. Results of the calculation are given below:

Case	Speeds ratio (v_A/v_B)	Observation range
R3 (A=NH_3, B=HCl), mode energy ($\hat{\varepsilon}$), virtual speed (s)	1.689	
R3 (A=NH_3, B=HCl), mode speed ($\hat{s}$), virtual speed (s)	1.636	
R3 (A=NH_3, B=HCl), average speed ($\bar{s}$), virtual speed (s)	1.616	
R3 (A=NH_3, B=HCl), average energy ($\bar{\varepsilon}$), virtual speed (s)	1.603	
R3 (A=NH_3, B=HCl), mode energy ($\hat{\varepsilon}$), real speed (v)	1.542	
R3 (A=NH_3, B=HCl), mode speed ($\hat{s}$), real speed (v)	1.494	
R3 (A=NH_3, B=HCl), average speed ($\bar{s}$), real speed (v)	1.475	
R3 (A=NH_4^+, B=Cl^-), average energy ($\bar{\varepsilon}$), real speed (v)	1.463	
R4 (A=NH_4^+, B=Cl^-), mode energy ($\hat{\varepsilon}$), virtual speed (s)	2.804	max ($v_B/(v_A+v_B) \approx 0.26$)
R4 (A=NH_4^+, B=Cl^-), mode speed ($\hat{s}$), virtual speed (s)	2.217	
R4 (A=NH_4^+, B=Cl^-), average speed ($\bar{s}$), virtual speed (s)	2.065	
R4 (A=NH_4^+, B=Cl^-), average energy ($\bar{\varepsilon}$), virtual speed (s)	1.983	
R4 (A=NH_4^+, B=Cl^-), mode energy ($\hat{\varepsilon}$), real speed (v)	1.983	
R4 (A=NH_4^+, B=Cl^-), mode speed ($\hat{s}$), real speed (v)	1.568	
R4 (A=NH_4^+, B=Cl^-), average speed ($\bar{s}$), real speed (v)	1.460	
R4 (A=NH_4^+, B=Cl^-), average energy ($\bar{\varepsilon}$), real speed (v)	1.402	min ($v_B/(v_A+v_B) \approx 0.42$)

Experimental apparatus

For the experiment of diffusion in gaseous state of the chemical species involved in formation of the ammonium chloride (HCl, Cl^-, NH_3, NH_4^+) are required a glass tube of (at least) 1m length and a diameter of about 2 cm. The tube must be dry. Are also required two rubber stoppers, two cotton pads, a horizontal fixing frame of the glass tube, and a timer for measuring a straight edge distance (see Fig. E5).

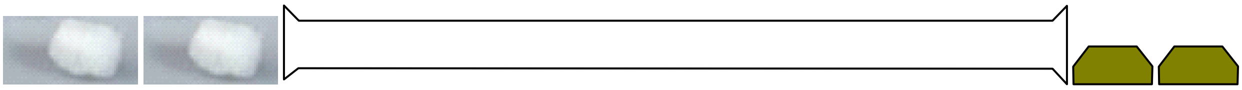


Fig. E5. Experimental apparatus for the study of diffusion in gaseous state

Working procedure

Assemble the experimental apparatus as shown in Fig. E6

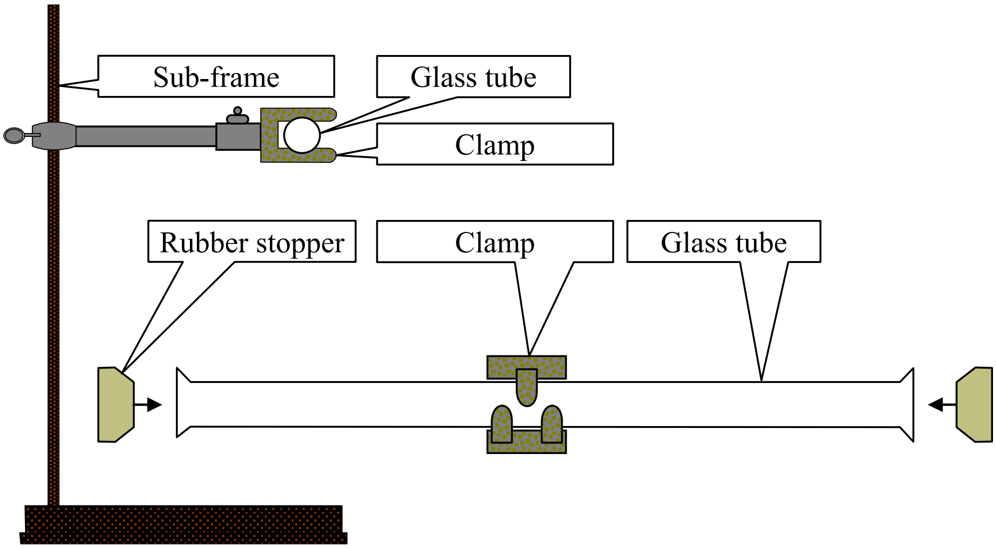


Fig. E6. The experimental setup for studying the gaseous diffusion

- The next steps are followed:
- The cotton swab is wetted in the solution of hydrochloric acid and other ammonia buffer solution;
- Are simultaneously placed on one side of the tube and the other two cotton pads, start the chronometer and put stoppers (v. Fig. E7);

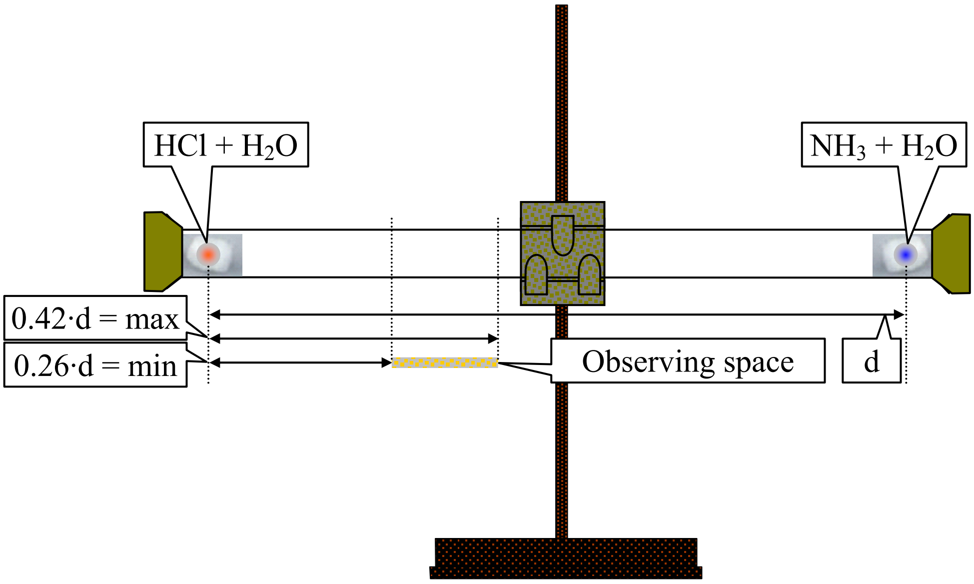


Fig. E7. Observation of the formation of ammonium chloride

- Ammonium chloride ring formation is observed; time is noted when (t_0);
- Measure the distance from the ring to the spot of ammonia; note this value (d_1);
- The distance from the ring to the spot of hydrochloric acid is measured; note this value (d_2);
- Take the value of the temperature in the laboratory; express it in K; note this value (T_1);

Data analysis

Two parameters were identical in the experiment: temperature (T_1) and the diffusion time (t_0).

- Is possible thus to calculate the diffusion speeds as well as their ratio. The following table is to be filled:

Chemical species	Distances (in m)	Time (in s)	Diffusion speeds (in m/s)	Speeds ratio
NH_3 or NH_4^+	$d_1 =$	$t_0 =$	$d_1/t_0 = v_1 =$	$v_1/v_2 =$
HCl or Cl^-	$d_2 =$		$d_2/t_0 = v_2 =$	

Table 3. Experimental data for the formation of the ammonium chloride

- Are compared the value of the diffusion speeds ratio with the value of the molecular speeds ratio with the purpose to decide which of the molecular speeds is responsible for the movement of the molecules in the process of diffusion. In order to do this, the values of the molecular speeds ratios (previous table) are sorted (ascending), are calculated the differences between these values and the value of the observed ratio and a seek for the lowest (absolute) difference is conducted (table 4 is to be filled; 'minimum' column will contain an entry for the smallest absolute value found):

Case	$\frac{v_A}{v_B}$	$\frac{v_A}{v_B}-\frac{v_1}{v_2}$	$\left\lvert\frac{v_A}{v_B}-\frac{v_1}{v_2}\right\rvert$	=minim
R4 (A=NH_4^+, B=Cl^-), average energy ($\bar{\varepsilon}$), real speed (v)	1.402			?
R4 (A=NH_4^+, B=Cl^-), average speed ($\bar{s}$), real speed (v)	1.460			?
R3 (A=NH_4^+, B=Cl^-), average energy ($\bar{\varepsilon}$), real speed (v)	1.463			?
R3 (A=NH_3, B=HCl), average speed ($\bar{s}$), real speed (v)	1.475			?
R3 (A=NH_3, B=HCl), mode speed ($\hat{s}$), real speed (v)	1.494			?
R3 (A=NH_3, B=HCl), mode energy ($\hat{\varepsilon}$), real speed (v)	1.542			?
R4 (A=NH_4^+, B=Cl^-), mode speed ($\hat{s}$), real speed (v)	1.568			?
R3 (A=NH_3, B=HCl), average energy ($\bar{\varepsilon}$), virtual speed (s)	1.603			?
R3 (A=NH_3, B=HCl), average speed ($\bar{s}$), virtual speed (s)	1.616			?
R3 (A=NH_3, B=HCl), mode speed ($\hat{s}$), virtual speed (s)	1.636			?
R3 (A=NH_3, B=HCl), mode energy ($\hat{\varepsilon}$), virtual speed (s)	1.689			?
R4 (A=NH_4^+, B=Cl^-), average energy ($\bar{\varepsilon}$), virtual speed (s)	1.983			?
R4 (A=NH_4^+, B=Cl^-), mode energy ($\hat{\varepsilon}$), real speed (v)	1.983			?
R4 (A=NH_4^+, B=Cl^-), average speed ($\bar{s}$), virtual speed (s)	2.065			?
R4 (A=NH_4^+, B=Cl^-), mode speed ($\hat{s}$), virtual speed (s)	2.217			?
R4 (A=NH_4^+, B=Cl^-), mode energy ($\hat{\varepsilon}$), virtual speed (s)	2.804			?

Table 4. Measuring agreement between the observation and the models- models sorted by speeds ratio

- Is identified the lowest absolute difference and thus are identified the chemical species which diffuses in gaseous state as well as the link between molecular speeds and diffusion speeds.
- The relations which characterize the model are written. These include the reaction of the formation of the ammonium chloride (R3 or R4), determinant factors in diffusion (energy or speed; real or virtual speeds; see also [150] and [151]) and expressions of the molecular speeds for the identified model;
- The coefficients of diffusion are calculated as ratios between diffusion speeds and molecular speeds: $c_1 = c(NH_3/NH_4^+) = v_1/v_A$; $c_2 = c(HCl/Cl^-) = v_2/v_B$, where v_A and v_B are the molecular speeds and their values depends on the obtained model; for instance when A = "NH_4^+", the best model agreeing with the experimental data is based on average energy ($\bar{\varepsilon}$) and real speed (v), then $v_A = v_{\bar{\varepsilon}}(NH_4^+) = 0.4196\cdot\sqrt{RT}$ (this is an example of calculation only; see Table 2);
- Following table should be filled:

Equation of the chemical reaction	F1: energy or speed	F2: real or virtual	Coefficients of diffusion
			c_1 =
			c_2 =

Table 5. Diffusion coefficients and the kinetic model for diffusion

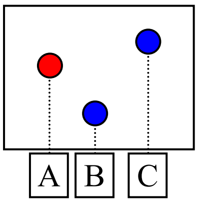
Further reading

Systems of particles and the rarefaction method

For a system S with N molecules having a number M of distinct energy states (let be N_1 molecules in the energy state ε_1, ..., N_M in the energy state ε_M; then $N = \Sigma_{1\le i\le M}N_i$). Sorting the energy states ($\varepsilon_1 < ... < \varepsilon_M$) does not affect the observation. Observing n out of N molecules exiting in the system, a question is raised: how many molecules should be observed (let's assume that the observation is simultaneous) such that the entire diversity of energy states to be captured?

Firstly, capturing of the whole diversity (M) is a matter of chance. Second, is obviously that is necessary at least $n \geq M$. Third, an isolated experiment affected or not by chance, will not characterize the system, while a repeating of it many times will assure that the (obtained) mean will be a sufficiency statistic [[152]] (see also [[68]]).

An example is useful. Let be a system with 3 molecules, one (A) being in the ε_1 energy state, and the other two (B and C) being in the ε_2 energy state (see figure below).



Choosing to observe 0 molecules, then for surely each time zero energy states are captured, and the mean is zero too. Similarly, observing one molecule, one energy state is captured each time and the mean is one too. If two molecules are observed, the chances to observe one of {A, B}, {A, C} and {B, C} are equal. In the first case ({A, B}) two energy states are captured, in the second ({A, C}) two again, and in the third ({B, C}) only one, thus the mean is (2+2+1)/3 ≈ 1.66. Only choosing to observe all three molecules each time, we are able to capture the true diversity of the energy states (2 energy states). This result is a more general one, coming from a Monte-Carlo [[153]] type experiment called the rarefaction method [[154]] (see also [[96]]).

Multinomial distribution by energies and maximization of the likelihood

Assuming that the molecules occupies a definite volume (V = constant) having different chances to posses a certain energy ε_k according to the rarefaction principle probability to have a certain arrangement (N_1, ..., N_k) by energy is given by the number of ways of selecting them. Expressing the probability from multinomial distribution, probability distribution comes from a certain arrangement (N_1, ..., N_k), which necessary is the result of a maximum chance to be observed. Applying thus the maximization of the likelihood (method established by Fisher, [[155]]; see also [[59]]):

$$\mathrm{PMF}(N_1,\ldots,N_K) = N!\cdot\prod_{j=1}^{K} p_j^{N_j} \Big/ \prod_{j=1}^{K} N_j!,\ \mathrm{MLE} = \ln(\mathrm{PMF}) = \ln(N!) + \sum_{j=1}^{K} N_j \cdot \ln(p_j) - \sum_{j=1}^{K} \ln(N_j!)$$

MLE function depends, for a N particle system, on N_1, ..., N_K values and the observation chance is maximized relative to these. Unfortunately these cannot vary independently, being the subject of two constrains, namely N is the total number of particles and E is the total (additive) energy of the system: $N = \Sigma_{1\leq j\leq k}N_j$ and $E = \Sigma_{1\leq j\leq k}\varepsilon_j\cdot N_j$. Thus the system can be solved applying the method of Lagrange's multipliers [[156]]: maximum points of MLE under constraints ($N - \Sigma_{1\leq j\leq K}N_j = 0$ and $E - \Sigma_{1\leq j\leq K}N_j\varepsilon_j = 0$) are found between the extreme points of (where α and β are constants to be determined reducing the number of variables):

$$\mathrm{MLE1}(N_1,...,N_k) = 1\ln(N!) + \sum_{j=1}^{K} N_j \cdot \ln(p_j) - \sum_{j=1}^{K} \ln(N_j!) + \alpha\left(N - \sum_{j=1}^{K} N_j\right) + \beta\left(E - \sum_{j=1}^{K} N_j \cdot \varepsilon_j\right)$$

Derivative of MLE1 relative to a variable (observable) N_i is:

$$0 \equiv \frac{\partial}{\partial N_i}\ln\left(N!\right) + \frac{\partial}{\partial N_i}\sum_{j=1}^{K}\ln\left(p_j^{N_j}\right) - \frac{\partial}{\partial N_i}\sum_{j=1}^{K}\ln\left(N_j!\right) + \frac{\partial}{\partial N_i}\alpha(N - \sum_{j=1}^{K} N_j) + \frac{\partial}{\partial N_i}\beta(E - \sum_{j=1}^{K}\varepsilon_j \cdot N_j)$$

and are fulfilled simultaneously for each i. It result thus a relation between N_i, their appearance probability p_i and their energy ε_i:

$$0 = \frac{\partial}{\partial N_i} N_i \ln(p_i) - \frac{\partial}{\partial N_i}\ln(N_i!) - \frac{\partial}{\partial N_i}\alpha(N_i) - \frac{\partial}{\partial N_i}\beta(\varepsilon_i \cdot N_i) \rightarrow \frac{\partial}{\partial N_i}\ln(N_i!) = \ln(p_i) - \alpha - \beta\varepsilon_i$$

where $\partial(\ln(\cdot))/\partial(\cdot)=\Psi(\cdot)$ is digamma function, α and β are the same for any i (being thus statistics of the distribution of the molecules by energy). Equation doesn't have an analytical solution for any x (N_i). Digamma function can be expressed using [157]:

$$\Psi(N_i + 1) = -\gamma + \sum_{j=1}^{N_i} 1/j \text{, or } 0 = \lim_{N_i \to \infty}\left(\Psi(N_i + 1) - \ln(N_i)\right)$$

where $\gamma = -\Psi(1)$ is the Euler's constant [158]. For large numbers ($N_i >> 1$) is possible to approximate to obtain a relationship between energy and the number of particles, Boltzmann [159] arriving to (solution retrieved using Stirling's approximation [160]):

$$\ln(N_i) = \ln(p_i) - \alpha - \beta\varepsilon_i \rightarrow N_i = p_i e^{-\alpha-\beta\varepsilon_i}$$

It should be noted that the previous formula is only an approximate one (see [82] and [83]).

Distribution by speed for an arbitrary number of energy components

By skipping some steps, it can be shown that the previous given formula may provide a distribution of the speeds for an energy component:

$$f(x) = a \cdot e^{-\pi a^2 x^2} \text{, where } a^2 = mN/(2\pi pV)$$

Assuming that the kinetic energy have J components ($\varepsilon = \varepsilon_1 + \varepsilon_2 + ... + \varepsilon_J$) and for each component a virtual (s) speed may be expressed along it ($\varepsilon_j = m \cdot s_j^2/2$), the value of the probability that a molecule to have s_1, s_2, ..., s_J as the components of the virtual speed is given by $dP = f(s_1)f(s_2)...f(s_J)d_{s1}ds_2...d_{sJ}$ and the mean of speed and the mean of square speed are given by the relations:

$$M(s) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}...\int_{-\infty}^{\infty}\sqrt{\sum_{j=1}^{J} s_j^2} \cdot \prod_{j=1}^{J} f(s_j) ds_1 ds_2 ... ds_J \text{ ; } M(s^2) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}...\int_{-\infty}^{\infty}\left(\sum_{j=1}^{J} s_j^2\right) \cdot \prod_{j=1}^{J} f(s_j) ds_1 ds_2 ... ds_J$$

It may be checked using substitution method that (the energy equipartition on its components):

$$M(s)=\frac{\Gamma\left(\frac{J}{2}+\frac{1}{2}\right)}{\Gamma\left(\frac{J}{2}\right)\pi^{1/2}a}=\frac{\Gamma\left(\frac{J}{2}+\frac{1}{2}\right)}{\Gamma\left(\frac{J}{2}\right)\sqrt{\frac{mN}{2pV}}};\ M(s^2)=\frac{\Gamma\left(\frac{J}{2}+1\right)}{\Gamma\left(\frac{J}{2}\right)\pi a^2}=J\cdot\frac{pV}{mN};\ E=N\cdot\frac{m\cdot M(s^2)}{2}=\frac{J}{2}\cdot pV$$

Ideal gas law and the relation between the temperature and the molecular speed

Synthesising a series of obtained results, were established that:

$$\frac{1}{3}M(v^2)=\frac{pV}{mN},\ \frac{\pi}{8}M^2(v)=\frac{pV}{mN},\ \frac{1}{J}M(s^2)=\frac{pV}{mN},\ \left(\frac{\Gamma(J/2)/\sqrt{2}}{\Gamma(J/2+1/2)}\right)^2 M^2(s)=\frac{pV}{mN}$$

where *v* is the real speed of the molecules, and *s* is the virtual speed of the molecules.

Experimentally the relation was checked and the demonstrative experiment were possible with the help of the thermometer assuring (keeping T = constant) the thermal equilibrium or tracing (when T varies) the energy transfer between systems and environment. By using the Kelvin scale for temperature, was shown that (where R, N_A and k_B are experimental constants: R = 8.3144621(75) J·K^{-1}·mol^{-1}, ideal gas constant; N_A = 6.02214129(27)·10^{23} mol^{-1}, Avogadro's number; k_B = 1.3806488(13)·10^{-23} J·K^{-1}, Boltzmann's constant): $pV = NRT/N_A = Nk_BT$.

A simple identification between terms can be done, taking into account that $m = M/N_A$ where M have the meaning of molar mass (contrasting with M(x) used here for mean of *x*), when it results:

$$\frac{1}{3}M(v^2)=\frac{RT}{M},\ \frac{\pi}{8}M^2(v)=\frac{RT}{M},\ \frac{1}{J}M(s^2)=\frac{RT}{M},\ \left(\frac{\Gamma(J/2)/\sqrt{2}}{\Gamma(J/2+1/2)}\right)^2 M^2(s)=\frac{RT}{M}$$

Obtaining of the oxygen: study of the gases laws

Introduction

Gaseous state is characterized by an internal energy from which most transforming part is kinetic energy. Very often, for small enough pressures and for high enough temperatures the gas is approximated as being an ideal one, using the relationship between its state parameters with:

$p \cdot V = n \cdot R \cdot T$	$R = 8.314$ J/mol/K	(Ideal)
$\rightarrow p \cdot M = \rho \cdot R \cdot T$		

A more exact treatment of the gaseous state is by involving the thermodynamic functions [161]. Anyway, obviously 'small enough' (for pressure) and 'high enough' (for temperature) depends on the chemical composition of the gas. For instance at 101325 Pa (1 atm) and 298 K (25 °C) O_2 is in gaseous state, S_8 is in solid state while H_2O is in liquid state. At a given pressure, as temperature become much higher than the vaporization temperature (of passing into gaseous state) with (about) the same the approximating error when is considered an ideal one it becomes smaller.

Often used approximations for the behaviour of a real gas are actually corrections applied to the ideal gas law by analytical formulas named virial, and expressed as is given in eq.1, where $B = B(T)$, $C = C(T)$ are functions of temperature and $V_m = V/n$ is the molar volume. Since higher order terms multiplying the inverse of the molar volume (C, ...) contributes increasingly less at the value (of the sum of), often is used the first approximation of the virial equation (eq.2).

The disadvantage of the virial equations is that the values of coefficients depend on the gas composition. To have an image of expressing the virial equations, please look at the virial equation for hydrogen (eq.3).

$p = \frac{RT}{V_m}(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ...)$	$p = \frac{RT}{V_m}(1 + \frac{B}{V_m})$	$B = \sum_{i=1}^{n} a_i \left(\frac{T_0}{T} - 1\right)^{i-1}$	$a_1 = 15.4$ $a_2 = -9.00$ $a_3 = -0.21$	H_2: $n = 3$, $T_0 = 298.15$ K
(eq.1)	(eq.2)	(eq.3)		

Other approximations are given by the relations implying the critical values for the pressure and temperature. Critical point, characterized by critical pressure, critical temperature and critical molar volume is the point from which ('from which' is regarding the temperature and the pressure) in general, doesn't exist any more phase frontier (in general; in particular, here is about the frontier between liquid and gaseous state). For instance, for water the phase frontier between liquid and gaseous states disappears when $T \geq T_C = 647$ K (374 °C) and $p \geq p_C = 22.064$ MPa (218 atm).

Anyway, there are many equations proposed to be used being in use today for the approximating of the real gases evolution. A part of these equations which are most often used are given in the next, for the purpose to be used in calculations as a part of the laboratory activity:

- Van der Waals [162] model:

$p=\frac{RT}{V_m-b}-\frac{a}{V_m{}^2}$	$a=\frac{27}{64}\frac{R^2T_C{}^2}{p_C}$, $b=\frac{1}{8}\frac{RT_C}{p_C}$	(Waals)
$\rightarrow \rho^3-\rho^2M/b+\rho M^2(RT+pb)/ab-pM^3/ab=0$		

- Abel-Noble [163] model:

$p=\frac{RT}{V_m-b}$	$b=\frac{1}{8}\frac{RT_C}{p_C}$	(Abel-Noble)
$\rightarrow \rho^{-1}=(RT)/(pM)+b$		

- Redlich-Kwong [164] model:

$p=\frac{RT}{V_m-b}-\frac{a}{V_m(V_m+b)T^{0.5}}$	$a=\frac{171}{400}\frac{R^2T_C{}^{2.5}}{p_C}$, $b=\frac{26}{300}\frac{RT_C}{p_C}$	(Redlich-Kwong)
$\rightarrow \rho^3+\rho^2M(RbT^{1.5}+pT^{0.5}b^2-a)/ab+\rho RT^{1.5}M^2/ab-pM^3T^{0.5}/ab=0$		

- Modified Berthelot [165] model:

$p=\frac{RT}{V_m}(1+a-ab)$	$a=\frac{9}{128}\frac{p/p_C}{T/T_C}$, $b=\frac{6}{(T/T_C)^2}$	(Berthelot)
$\rightarrow pM=\rho RT(1+a-ab)$		

- Clausius [166] model:

$p=\frac{RT}{V_m-b}-\frac{a}{T(V_m+c)^2}$	$a=\frac{27}{64}\frac{R^2T_C{}^3}{p_C}$, $b=V_C-\frac{RT_C}{4p_C}$, $c=\frac{3}{8}\frac{RT_C}{p_C}-V_C$	(Clausius)
$\rightarrow \rho^3+\rho^2\frac{M(2RT^2c+2pTbc-pTc^2-a)}{ab+RT^2c^2+pTbc^2}+\rho\frac{TM^2(RT+pb-2pc)}{ab+RT^2c^2+pTbc^2}-\frac{pTM^3}{ab+RT^2c^2+pTbc^2}=0$		

- Wohl [167] model:

$p=\frac{RT}{V_m-b}-\frac{a}{TV_m(V_m-b)}+\frac{c}{T^2V_m{}^3}$	$a=6p_CT_CV_C{}^2$, $b=\frac{V_C}{4}$, $c=4p_CT_C{}^2V_C{}^3$	(Wohl)
$\rightarrow \rho^4-\rho^3\frac{M}{b}+\rho^2\frac{aTM^2}{bc}-\rho\frac{T^2M^3(pb+RT)}{bc}+\frac{pT^2M^4}{bc}=0$		

The disadvantage of the state equations (given above) for the real gases consists in the fact that the constants implied in the models having an expression depending on the critical parameters can be obtained only for pure gases, and thus for mixtures the values of the constants implied in models should be experimentally determined. For instance for air the values of the Van der Waals model constants are $a = 0.1358$ and $b = 3.64\cdot10^{-5}$.

In the laboratory it is easily to obtain pure oxygen through thermal decomposition of the oxygen rich containing salts, thus being useful the constants of the models for it (for oxygen).

Purpose

The experiment will be conducted operationalizing the mass conservation principle and thus comparing of the experimental results with the ones coming from the applying of the gases equations of state. It will be studied the oxygen produced from the decomposition of a potassium salt.

Material and method

In the presence of a catalyst (here MnO_2 will be used) occurs relatively fast the thermal decomposition of the potassium chlorate in potassium chloride when oxygen are released, as is given by the equation of the chemical reaction:

$$KClO_3 \rightarrow KCl + {}^3/_2O_2\ (MnO_2, t°C)$$

For the values of the critical constants, ref. [168] should be used. Here is a series of values:

Substance	T_C (K)	p_C (MPa)	$V_{C,m}$ (cm^3/mol)
Oxygen (O_2)	154.59	5.043	73
Ozone (O_3)	261.1	5.57	89
Nitrogen (N_2)	126.21	3.39	90
Water (H_2O)	647.14	22.06	56
Carbon dioxide (CO_2)	304.3	7.375	94
Sulphur dioxide (SO_2)	430.64	7.884	122
Argon (Ar)	150.87	4.898	75
Hydrogen (H_2)	32.97	1.293	65
Helium (He)	5.19	0.227	57
Carbon monoxide (CO)	132.86	3.494	93
Methane (CH_4)	190.56	4.599	98.6
Octane (C_8H_{18})	568.7	2.49	492

For the values of the virial coefficients a call for a catalogue of physical and chemical constants can be pursued, as is CRC [169]. Here a list of values is given (for $p·V_m^2 = RT(V_m + B)$; $B = \Sigma_i a_i(T_0·T^{-1} -1)^{i-1}$, $T_0 = 273.15$ K):

Substance	Coefficients
Oxygen (O_2)	$a_1 = -16$; $a_2 = -62$; $a_3 = -8$; $a_4 = -3$
Carbon dioxide (CO_2)	$a_1 = -127$; $a_2 = -288$; $a_3 = -118$
Carbon monoxide (CO)	$a_1 = -9$; $a_2 = -58$; $a_3 = -18$
Methane (CH_4)	$a_1 = -43$; $a_2 = -114$; $a_3 = -19$; $a_4 = -7$
Sulphur dioxide (SO_2)	$a_1 = -430$; $a_2 = -1193$; $a_3 = -1029$
Water (H_2O)	$a_1 = -1158$; $a_2 = -5157$; $a_3 = -10301$; $a_4 = -10597$; $a_5 = -4415$
Helium (He)	$a_1 = 12.44$; $a_2 = -1.25$
Ammonia (NH_3)	$a_1 = -271$; $a_2 = -1022$; $a_3 = -2715$; $a_4 = -4189$
Argon (Ar)	$a_1 = -16$; $a_2 = -60$; $a_3 = -9.7$; $a_4 = -1.5$

For the general form of the virial model, Wagner & collaborators [170] determined the expressions of the first and of the second virial coefficient for oxygen, the result being given in the next table.

<table>
<tr><td colspan="2">$p = (1 + B·V_m + C·V_m^2)·V_m·R·T$</td><td rowspan="3">(Wagner)</td></tr>
<tr><td colspan="2">$B = b_1 + b_2·T^{-0.25} + b_3·T^{-3.5} + b_4·T^{-4.5} + b_5·T^{-5.5}$</td></tr>
<tr><td colspan="2">$C = c_1·T^{-0.25} + c_2·T^{-6} + c_3·T^{-6.75}$</td></tr>
<tr><td colspan="2">For T in K, B in dm^3/mol and C in $(dm^3/mol)^2$:</td><td rowspan="4">Oxygen</td></tr>
<tr><td>$b_1 = 0.143389$</td><td>$c_1 = 0.451336·10^{-2}$</td></tr>
<tr><td>$b_2 = -0.629863$</td><td>$c_2 = 0.987169·10^{11}$</td></tr>
<tr><td>$b_3 = -0.577814·10^7$</td><td>$c_3 = -0.364928·10^{13}$</td></tr>
</table>

$b_4 = 0.695858 \cdot 10^9$		
$b_5 = -0.246023 \cdot 10^{11}$		

To simplify the processing of data were calculated the Van der Waals coefficients for oxygen ($a = 1.382 \cdot 10^{-5}$ dm^6/mol^2 and $b = 0.0319$ dm^3/mol) and ozone ($a = 3.570 \cdot 10^{-5}$ and $b = 0.0487$).

Experimental apparatus

To conduct the experiment are necessary (see Fig. 1): working table, a beaker or a flask of any type, a test tube, a large round bottom flask (with at least two necks), three perforated rubber stoppers and traversed with glass tubes (one with a long tube), two rubber hoses, support for the large round bottom flask, gas burner, elevating system for the gas burner, supporting frame and fixing clamps for sustaining the test tube (last ones not depicted in Fig. 1).

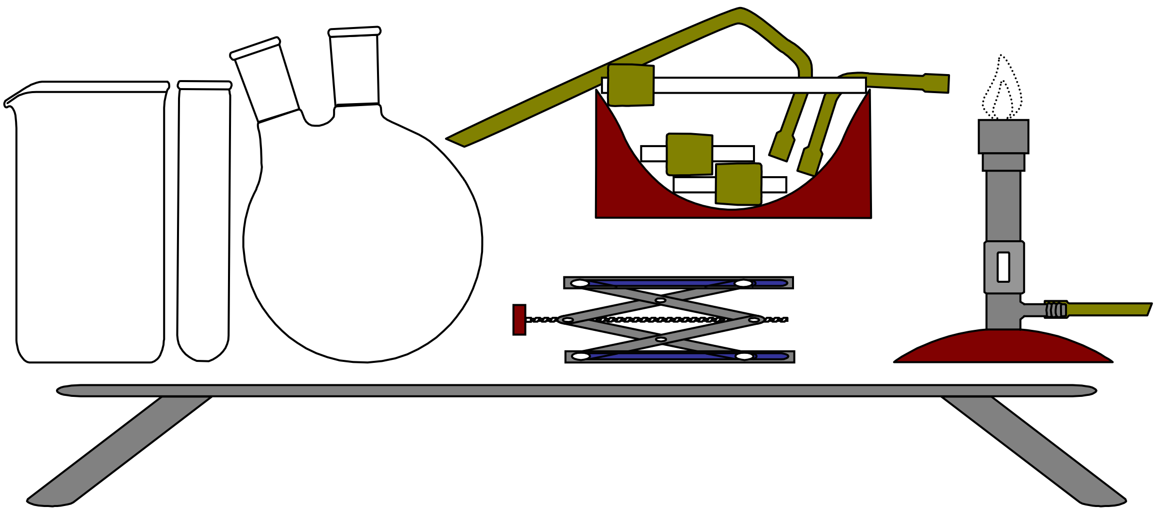
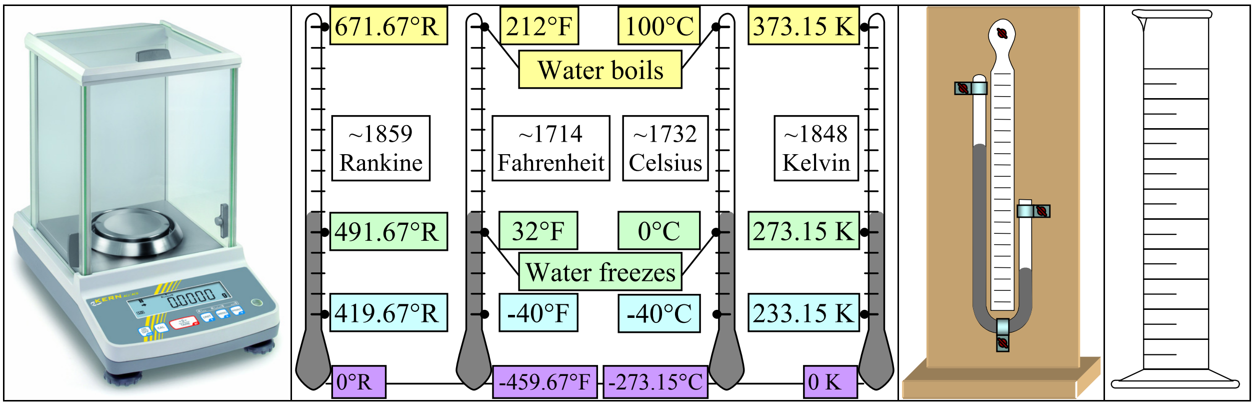


Fig. E1. Experimental apparatus

As supplementary to the experimental apparatus (given in figure E1) are required to an analytical balance, a barometer, a thermometer and a graduated cylinder, all being part of the equipment of the laboratory where experiments are conducted.



Working procedure

Is assembled the experimental apparatus like in Fig. E2 (test tube is immobilized with the fixation clamps on the supporting frame).

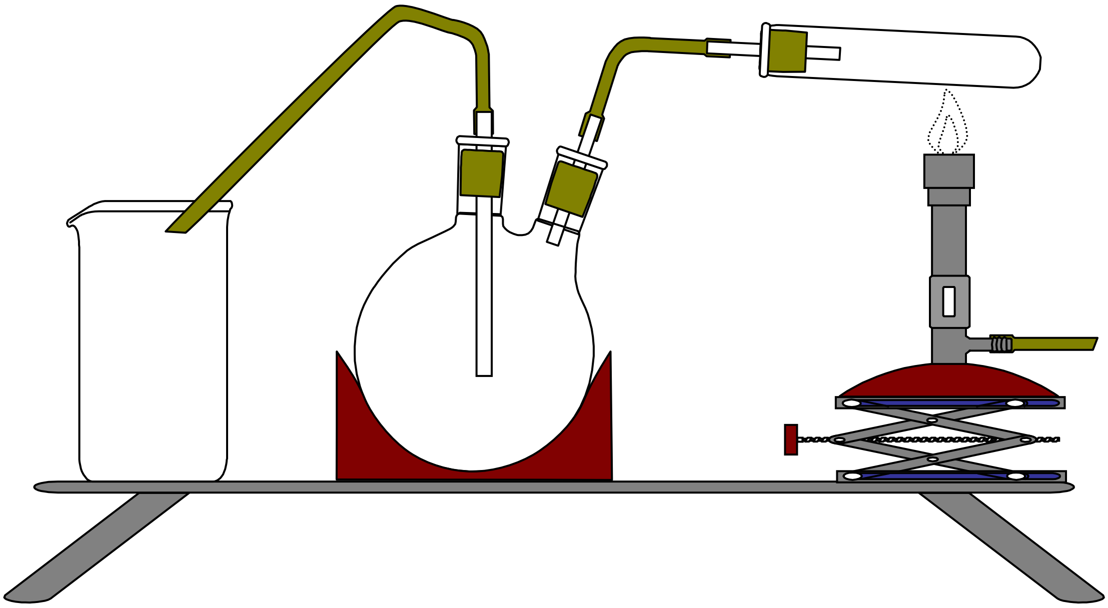


Fig. E2. The construction of the experiment for the study of the gases laws

The next steps are followed:

- ÷ The tube is detached and weighed; note its mass (m_1);
- ÷ In the tube is inserted approximately 1g of $KClO_3$ and in trace MnO_2 (catalyst); reweigh the tube; note its mass (m_2);
- ÷ Fix the tube; power on the gas burner; ensure that all terminals attached to the rubber hoses are open so that the overpressure is not created;
- ÷ Approach the gas burner to the test tube and heat the region in the vicinity of the sample (see Fig. E3); wait until the temperature is high enough to trigger the decomposition reaction;

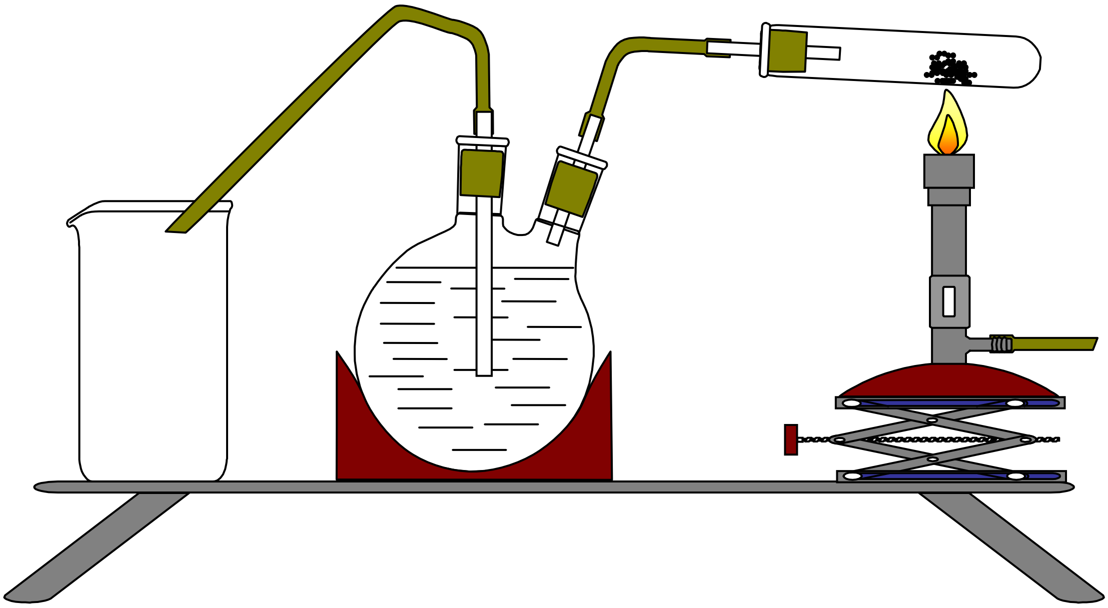


Fig. E3. Initiation of the thermal decomposition

- ÷ Once reached the temperature initiating the thermal decomposition, the reaction occurs fast and therefore from this point on the gas burner can be removed safely (see Fig. E4);

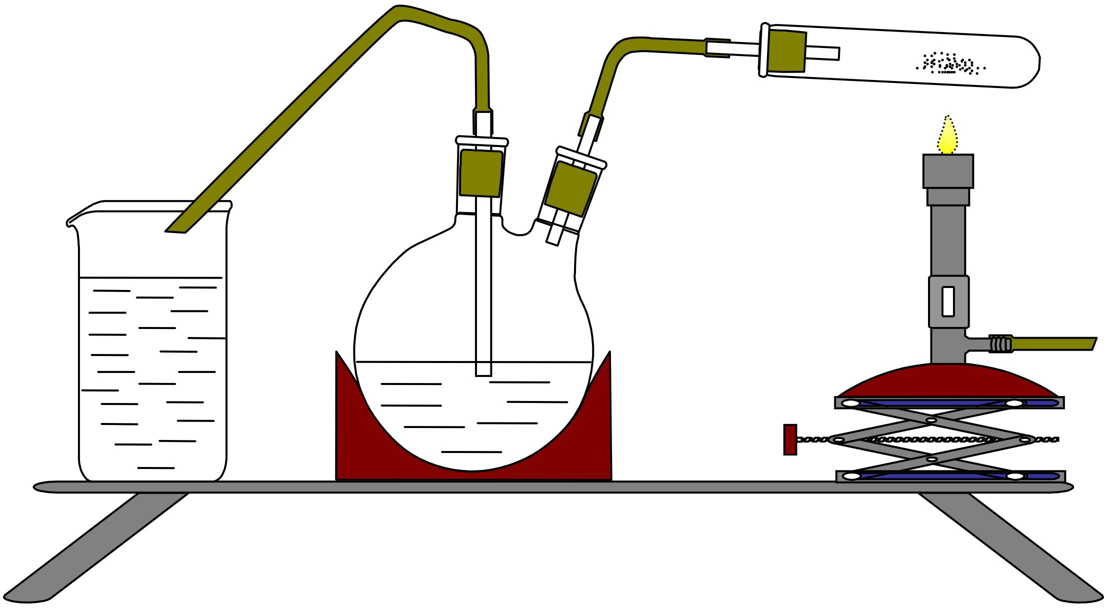


Fig. E4. The end of the thermal decomposition

- The gas burner is to be powered off and the clamps from the rubber hoses are to be closed; are waited to be cooled down the test tube; the test tube is weighted; note its mass (m_3);
- Is measured the volume of the water replaced in the large round bottom flask by the oxygen from the decomposition reaction, water which is now in the Berzelius beaker; note its volume (V_1);
- Temperature in the laboratory is recorded from the thermometer; note its value (t_1);
- Pressure in the laboratory is recorded from the barometer; note its value (P_1);

Data analysis

- If t_1 is the temperature from the thermometer (in Celsius degrees), then $T_1 = t_1 + 273.15$ (in Kelvin). If P_1 is the pressure from the barometer (in mmHg), then $p_1 = 101325 \cdot P_1/760 = 133.322 \cdot P_1$ (in N/m^2). The values are written in the table:

Experiment	t_1 (°C)	T_1 (K)	P_1 (Torr)	p_1 (N/m^2)
Date:Time				

Is expressed the mass balance using the equation of the chemical reaction:

Reaction	m_2-m_1		m_3-m_1		m_3-m_2	→	n
R_1:	$KClO_4 + MnO_2$	→	$KCl + MnO_2$	+	$^3/_2O_2$		$n(O_2) = (m_3-m_2)/M(O_2)$; $M(O_2) = 32$ g/mol
R_2:	$KClO_4 + MnO_2$	?	$KCl + MnO_2$	+	$2O_3$		$n(O_3) = (m_3-m_2)/M(O_3)$; $M(O_3) = 48$ g/mol

- Is calculated the quantity of released gas (oxygen or ozone) assuming the two possible reactions. By taking into consideration that it exists, deviations from the ideal gas are small, the volume of the released gas is used in order to decide which reaction took place (R_1 or R_2): $n_1 = (p_1 \cdot V_1)/(R \cdot T_1)$
- Obtained values are written in the following table and are concluded about the chemical reaction which took place:

?	n_1 (mol)	$n(O_2)$ (mol)	$n(O_3)$ (mol)
Values			
Conclusion:			

- It's possible that the values to be different, one possible cause being the experimental error, other being the deviation from the ideal gas law; the magnitude of the error will be assessed relative to the models.

Looking at the experimental design (see fig. E3 and E4) that the highest measurement error may appear from the neglecting of the effect of the water column from the ascending tube (and the pressure from the round flask in which the oxygen are released to be higher than the atmospheric pressure). As consequence the previous given models will be used to assess the deviation between the observed (on barometer) pressure and calculated (from models) one. For each model is conducted the calculation and the results are to be written in the next table (the observed values are to be used as it follows):

V_m		p	T	R
V_1/n_1		p_1	T_1	8.314
______ [in m^3]	______ [in dm^3]	______ [in N/m^2]	______ [in K]	[in J/mol/K]

- Using these values, calculate and decide which error is the smallest one:

Model	Formula	Coefficients	Calculation result
Ideal	$\varepsilon_I = p - \frac{RT}{V_m}$	-	$\varepsilon_I =$
Van der Waals	$\varepsilon_{vdW} = p - \frac{RT}{V_m - b} + \frac{a}{V_m^2}$	$a = 1.382 \cdot 10^5\ (dm^3/mol)^2$ $b = 0.0319\ (dm^3/mol)$	$\varepsilon_{vdW} =$
Abel-Noble	$\varepsilon_{A-N} = p - \frac{RT}{V_m - b}$	$b = 0.0319\ (dm^3/mol)$	$\varepsilon_{A-N} =$
Redlich-Kwong	$\varepsilon_{R-K} = p - \frac{RT}{V_m - b} + \frac{a}{V_m(V_m + b)T^{0.5}}$	$a = 1.741\ (m^3/mol)^2$ $b = 2.21 \cdot 10^{-5}\ (m^3/mol)$	$\varepsilon_{R-K} =$
Clausius	$\varepsilon_C = p - \frac{RT}{V_m - b} + \frac{a}{T(V_m + c)^2}$	$a = 21.363\ (K \cdot (m^3/mol)^2)$ $b = 9.285 \cdot 10^{-6}\ (m^3/mol)$ $c = 2.257 \cdot 10^{-5}\ (m^3/mol)$	$\varepsilon_C =$
Wohl	$\varepsilon_W = p - \frac{RT}{V_m - b} + \frac{a}{TV_m(V_m - b)} - \frac{c}{T^2 V_m^3}$	$a = 24.93$ (SI units) $b = 1.825 \cdot 10^{-5}$ (SI units) $c = 0.188$ (SI units)	$\varepsilon_W =$
Virial 1	$\varepsilon_{V1} = p - \frac{RT}{V_m}\left(1 + \frac{1}{V_m}\sum_{i=1}^{4} a_i \left(\frac{273.15}{T} - 1\right)^{i-1}\right)$	$a_1 = -16$; $a_2 = -62$; $a_3 = -8$; $a_4 = -3$	$\varepsilon_{V1} =$
Virial 2	$\varepsilon_{V2} = p - (V_m + BV_m^2 + CV_m^3)RT \cdot 10^{-3}$	V_m in dm^3/mol $b_1..b_5$ and $c_1..c_3$ cf. Wagner	$\varepsilon_{V2} =$

Provide an answer to the following questions:

- Whish model is the best approximate for the experimental observation?
- Which is the magnitude of the relative error (percent one)?
- Is better to inflate tires with nitrogen (N_2) than with air? Why?

Further reading: Equilibrium state and state parameters

A state to be characterized as of equilibrium state assumes assessing of the mechanical, thermal, and chemical equilibrium. At least the definition of the chemical equilibrium assumes the existence of a stationary state (in time) and from this point of view an immediate consequence is the reflexivity of the equilibrium: if A is in equilibrium, then A is in equilibrium with A. Also the symmetry of the equilibrium must be accepted: if A is in equilibrium with B, then B is in equilibrium with A. More, the transitivity is assured too ("zero's principle of the thermodynamics"): if A in equilibrium with B, and B in equilibrium with C, then A is in equilibrium with C, thus the equilibrium concept defines an equivalence relation between systems (see next figure; the concept of equilibrium is at the basis of the construction of many instruments, including the thermometer).

Reflexive	A (EQ) A
Symmetric	If [A (EQ) B] then [B (EQ) A]
Transitive	If [A (EQ) B] & [B (EQ) C] then [A (EQ) C]
Equivalence	(EQ) Reflexive & Symmetric & Transitive

A state is defined generally using a series of its observable properties. To be remembered is that the necessary number of parameters to define a state of a system depends on the system and being not generally known. Defining of a property as a state parameter is directly linked by our capacity to observe it on the systems being in equilibrium. State parameters can be categorized as is shown in the next:

⊞ State parameters			
⊟ Structure	⊟ Energy	⊟ Quantity	⊟ ? ...
Density (ρ)	Temperature (T)	Mass (m)	...
Pressure (p)	Internal energy (E)	Volume (V)	
Molar mass (M)	Enthalpy (H)	Particle's number (N)	
Entropy (S)	Gibbs's free energy (G)	...	
Chemical composition (F)	Helmholtz's free energy (H)		
Fugacity (f)	Exergy (B)		
...	...		

Characteristic to the state parameters (or functions) is that it not depends on the succession of processes through the system evolved to arrive at. In other words, any closed path followed by a process will bring the system in the same state, characterized by the same values for the state parameters. By contrast, all parameters depending on the succession of the processes through which system evolved enter in the category of parameters of process. Thus, work (mechanical, electrical) and heat are parameters of process.

Qualitative analysis of metals and alloys

Introduction

There are many methods for analyzing samples containing metals, some of them conducting the analysis with the sample in solid state or after passing the metals into a solution as cations.

With regard to the 'qualitative' word meaning, a qualitative method is intended to be used to provide a 'Yes/No' answer to the question if a (certain) metal is present in the sample, while a quantitative method is intended to be used to provide a quantity (with measurement units such as mass or volume) or a ratio (or a percentage) of representation of the metal in the sample. It exists also methods called 'semi-quantitative' of which intend is to be used as prerequisite for the other two categories.

Other classification of the methods takes into consideration the size of the (required) sample, and from this point of view, the methods may be intended for macro (quantities) when the size is about 100mg, semi-micro (size about 10 mg), micro (~ 1 mg), ultra-micro (~ 1 μg) and sub-micro (~ 10 ng).

Chemical methods are generally involved for macro-quantities, while instrumental methods are for micro-quantities. The modern apparatus for analysis generally couple chemical with instrumental methods to provide both qualitative and quantitative information about the composition of the samples.

Other partition on the set of the analysis methods divide the methods in destructive (when a part of or whole sample suffers irreversible changes during the analysis) and nondestructive (when no changes or reversible changes are applied to a part or whole sample).

Some of the methods provide an information correlated with the quantity (of the metal in the sample), and then are called absolute or stoechiometric methods while others provide an information correlated with the ratio (or proportion of the metal in the sample), and then are called relative or non-stoechiometric methods, tracing the metals being an important issue in environmental science [171].

The experiment which will be conducted in the laboratory it uses an apparatus to disrupt from the surface of the sample the metals and to pass it into a solution as cations with the help of the continuous electric current. The device is sometimes called electrograph, but due to simplicity of its use is better called metal ionizer.

Purpose

The purpose of the laboratory activity is to qualitatively analyze a series of metallic samples. Therefore, each student will analyze one sample.

Material and method

The principle of analysis works the same at this device as it works for a modern device which is able to identify the metals based on their oxidation potential, and then the metal ionizer is coupled in an electric circuit with an adjustable voltage source (usually with a feature producing a known potential-time curve) as well as with a potential-intensity-time recording device.

The metallic sample is placed between the plates of the metal ionizer, and between the sample and the positive charged plate is placed a filter paper moistened with a solution of containing NO_3^- anions. Connecting the device to the power source operating with a potential in 2-6V range will pass atoms of the metals from the sample to the filter paper as cations combining it with the NO_3^- anions:

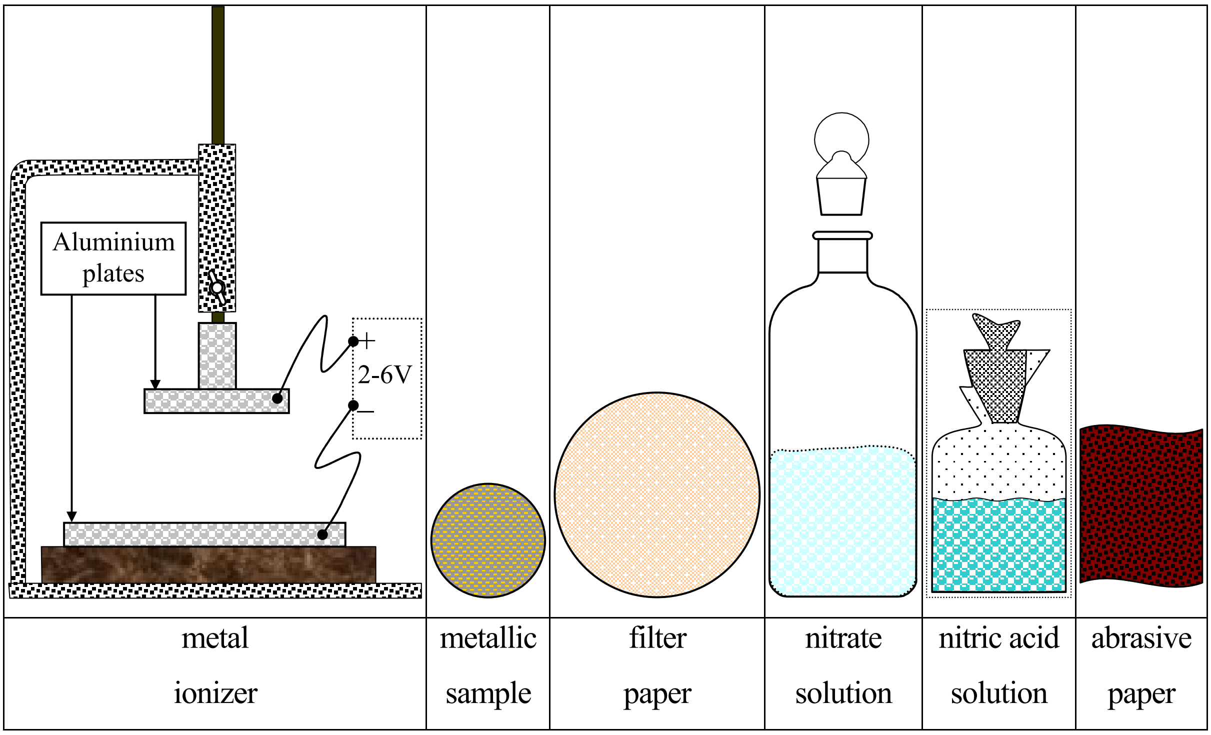
$Me^0 - ne^-$	$\rightarrow$	Me^{n+}
Sample (containing Me^0) is connected at anode (+), passing thus the electrons (ne^-) through the electric circuit		Filter paper (containing Me^{n+}) is connected at cathode (-), allowing the metallic cations to migrate to it and discharge on it

It's a general rule that salts containing nitrate ion (NO_3^-) are soluble. Other discharges are possible too at the cathode, for the other ions present in the solution. Thus, writing the dissociation of the water, it is clear that also hydrogen ions (named 'hydron') may discharge. Which ion actually discharge it depend on the oxidation potential of the metal (and for the competition with hydron, if this potential is positive or not; a negative electrode potential indicate that hydrogen discharge in the place of the metallic cation).

$H_2O \leftrightarrow H^+ + HO^-$	$2H^+ + 2e^- \rightarrow H_2$	$Me^{n+} + ne^- \rightarrow Me^0$
water dissociation	possible reactions at cathode	

As can be seen from the previous table, consuming of the hydrons from the water may lead to a basic solution (with a pH greater than 7), when the cations of the metal may combine with hydroxide (HO^-) to form hydroxides ($Me(OH)_n$). This is an unwanted outcome, because most of the hydroxides are only slightly soluble, and we need to have soluble combinations of the cations from at least two reasons: to keep the conduction of the current trough the circuit long enough to pass as many as possible metallic cations on the filter paper as well as for the next stage, analysis of the metallic cations with a series of specific reactions is necessary to have soluble compounds of it in order to make possible the aqueous reaction with the reagents.

To conduct one experiment of sample analysis, is necessary the sample, some abrasive paper to polish the sample (some metals oxidizes in the presence of air and moisture, covering itself with an isolating layer of oxide and/or hydroxide), a filter paper, a nitrate solution (usually 5% $NaNO_3$), a nitric acid solution (usually diluted HNO_3), of the metal ionizer along with the power source (see the next figure) as well as a series of reagents to conduct the specific reactions for cations identification.

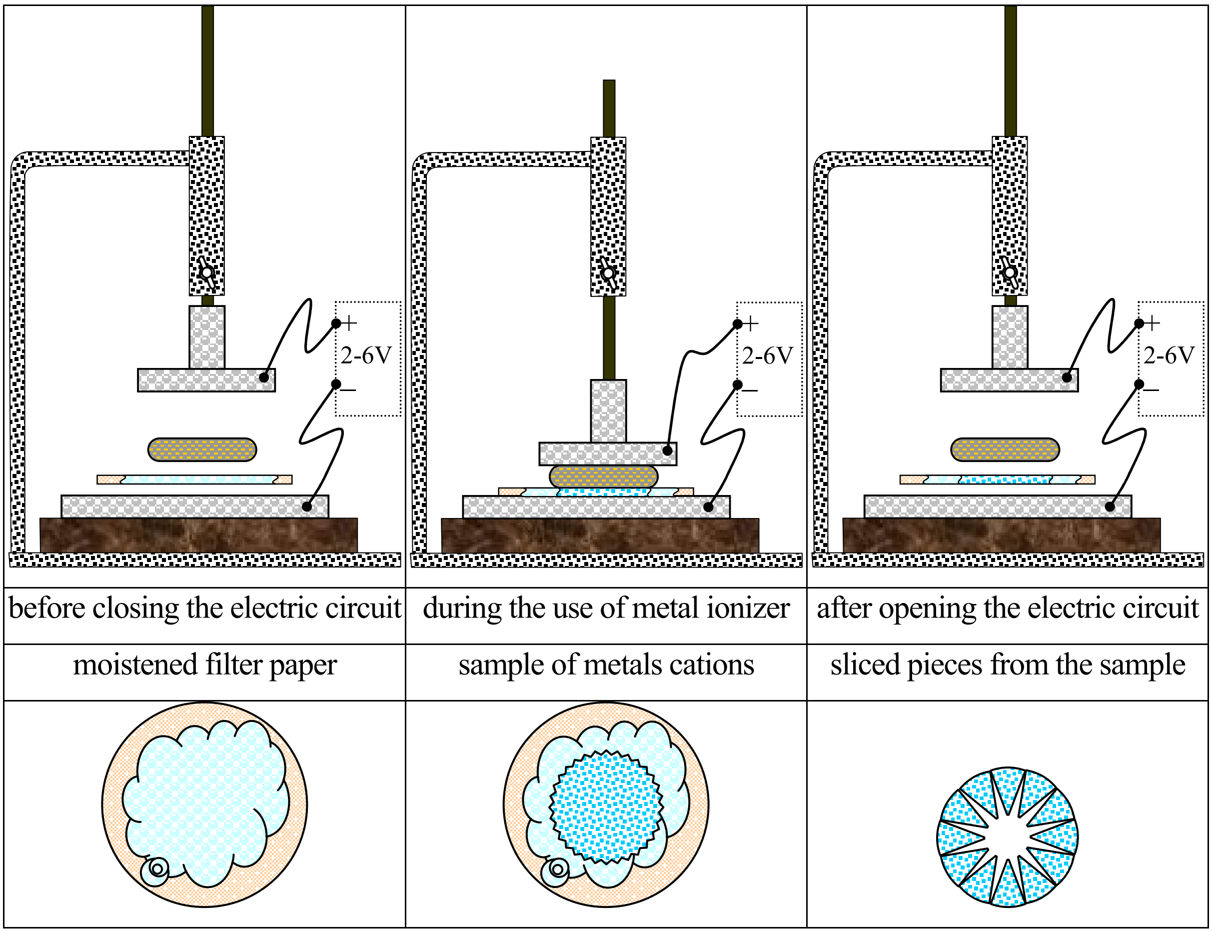


Working procedure

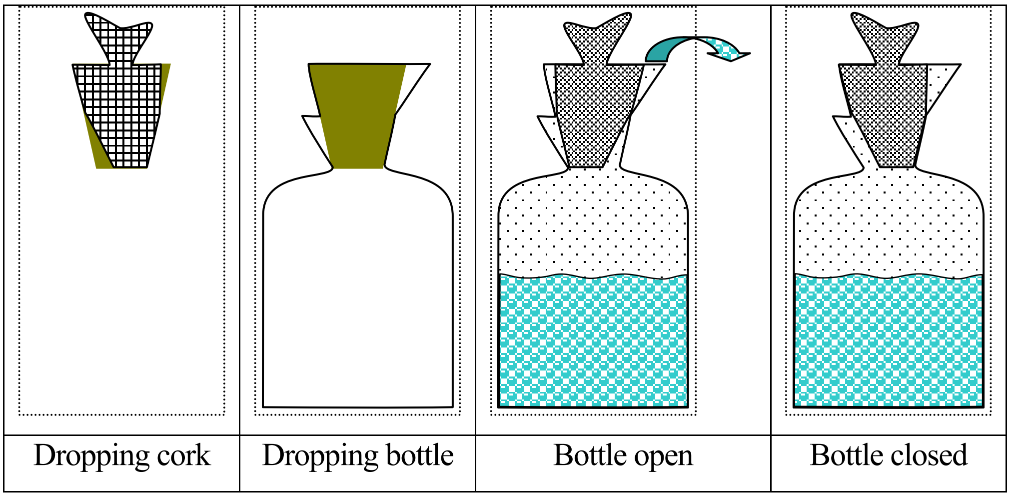
The succession of the steps is as follows:

- Eventually degrease the sample with milk of lime ($Ca(OH)_2$);
- Polish the metallic sample with abrasive paper;
- Eventually using a pencil divide the filter paper in at least eight parts, to be used each to analyze a certain cation;
- Moist the filter paper with nitrate solution;
- Add (on the filter paper) few drops of nitric acid;
- Clean the plates of the metal ionizer from possible foreign ions using a piece of paper (regular paper, filter paper or abrasive paper if is necessary);
- Place the moistened filter paper on the cathode (bottom plate), the sample over it and use the screw to come down the anode (upper plate) over the sample;
- Turns on the power source; press on the upper plate if is necessary to keep the electrical circuit till a clear trace of the sample remains on the filter paper; turn off the power source; repeat this step if necessary to obtain a uniform diffusion of the metallic ions in the filter paper;
- Rise up the anode; take up the metallic sample; take up the filter paper containing the cations to be analyzed;
- Eventually use a scissor (but not a metallic one, because it may contaminate with foreign ions the analysis) to cut the filter paper in pieces;
- Conduct the series of specific reactions for each cation corresponding to the following metals: Fe,

Co, Ni, Cr, Cu, Pb, Al, Zn (eventually use a lamella of glass for);



Experimental procedure with the metal ionizer



Structure and usage of dropping bottle

Identification of the cations

- A series of specific reactions of identification for the Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, and Al^{3+} cations will be conducted;
- One positive reaction is enough for identification of the presence of a metal in the sample;
- Before to proceed with the reactions, based on the notes given in the table below as well as based on the available reagents a plan of conducting the cations identification (which reactions and in

which succession) should be written;

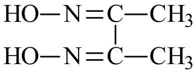
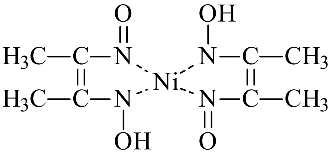
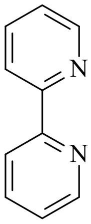
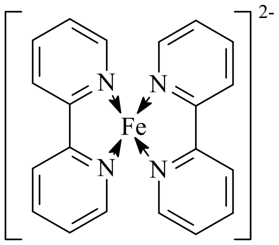
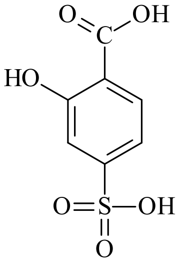
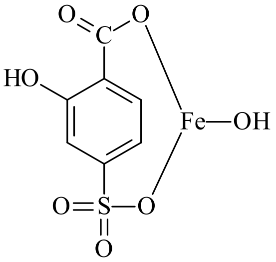
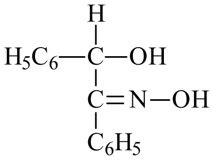
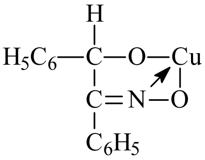
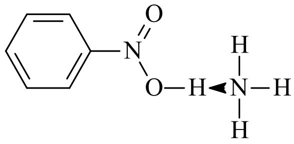
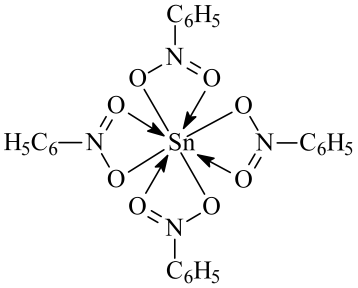
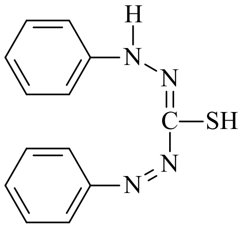
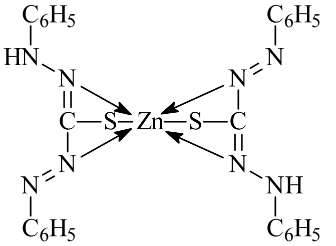
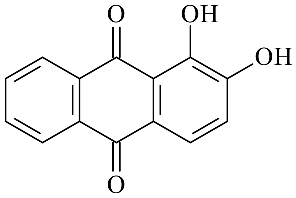
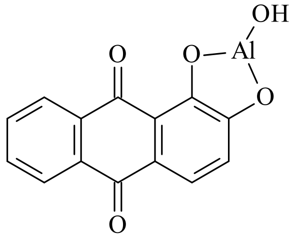
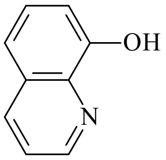
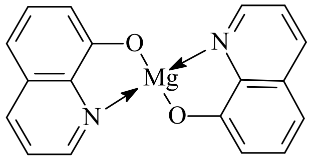
÷ The series of the reactions is in the following table:

Cation	+	Reagents	→	Products	Color	Note
Fe^{2+}	+	$K_3Fe(CN)_6$	→	$Fe_3[Fe(CN)_6]_2 + K^+$	blue	1
	+	NaOH	→	$Fe(OH)_2 + Na^+$	gray-green $\xrightarrow{air}$ red-brown	
	+	DMG	→	$Fe(DMG)_2 + H^+$	red	
	+	Dipyridile	→	$Fe(dipyridile)_2^{2+}$	purple red	
Fe^{3+}	+	$K_4Fe(CN)_6$	→	$Fe_4[Fe(CN)_6]_3 + K^+$	blue	2
	+	NH_4OH	→	$Fe(OH)_3 + NH_4^+$	reddish brown	3
	+	NH_4SCN	→	$Fe(SCN)_3 + NH_4^+$	red	4
	+	CH_3COONa	→	$Fe(CH_3COO)_3 + Na^+$	red-brown	
	+	$CH_3COONa + KI$	→	$Fe(CH_3COO)_2 + I_2 + Na^+ + K^+$	brown	
	+	Sulphosalicylic acid	→	Fe(sulphosalicylate) + H^+	at $pH\in[1.8,2.5]$, red-violet	
Co^{2+}	+	NH_4SCN	→	$Co(NH_4)_2(SCN)_4 + NH_4^+$	blue	4
	+	NH_4OH + DMG	→	$Co(DMG)_2 + H^+ + H_2O$	dark brown	5
	+	$NO_3^- + Al_2(SO_4)_3$	→	$Co(AlO_2)_2 + NO_2 + O_2 + SO_3$	Tenard's blue at ignition	6
	+	$NO_3^- + Zn(NO_3)_2$	→	$CoZnO_2 + NO_2 + O_2$	Rinmann’s green at ignition	7
	+	$NH_4OH + H_2O_2$	→	$Co(NH_3)_5^{3+} + H_2O$	red	
	+	NaOH	→	$Co(OH)^- \xrightarrow{heating} Co(OH)_2 \xrightarrow{air} Co(OH)_2^{1+}$	dark blue $\xrightarrow{heating}$ rose $\xrightarrow{air}$ brown	
Cu^{2+}	+	NH_4OH	→	$Cu(NH_3)_4(OH)_2 + H^+ + H_2O$	intense blue	3
	+	$K_4Fe(CN)_6$	→	$Fe_4[Fe(CN)_6] + K^+$	red-brown	2
	+	Cuprone	→	Cu(cuprone) + H^+	dark green $\xrightarrow{flame}$ dark blue or green	
Pb^{2+}	+	KI	→	$PbI_2 + K^+$	yellow	
	+	K_2CrO_4	→	$PbCrO_4 + K^+$	yellow	
Sn^{4+}	+	Cupferron + NH_4OH	→	$Sn(cupferron)_4 + H^+ + H_2O$	yellow	
Zn^{2+}	+	$K_3Fe(CN)_6$	→	$Zn_3[Fe(CN)_6]_2 + K^+$	white to green when heated	1
	+	$NO_3^- + Co(NO_3)_2$	→	$CoZnO_2 + NO_2 + O_2$	Rinmann’s green at ignition	7
	+	Dithizone	→	$Zn(dithizone)_2 + H^+$	red	8
Cr^{3+}	+	NH_4OH	→	$Cr(OH)_3 + NH_4^+$	gray-green	3
	+	H_2O_2 (+ NaOH)	→	$(CrO_4)^{2-} + H_2O\ (+ Na^+)$	yellow	
	+	H_2O_2 (+ HCl)	→	$H_2Cr_2O_7 + H^+ + H_2\ (+ Cl^-)$	orange	
Ni^{2+}	+	NH_4OH	→	$Ni(NH_3)_6(OH)_2 + H^+ + H_2O$	blue	3
	+	NH_4OH + DMG	→	$Ni(DMG)_2 + H^+ + H_2O$	red	5
	+	Na_2HPO_4	→	$Ni_3(PO_4)_2$	green	
Al^{3+}	+	NH_4OH	→	$Al(OH)_3 + NH_4^+$	white gelatinous	3
	+	Alizarin + NH_4OH	→	$Al(alizarin)_3 + H_2O + NH_4^+$	red	
	+	Oxyne	→	$Al(oxyne)_3 + H^+$	yellow	
Mg^{2+}	+	Oxyne + NaOH	→	$Mg(oxyne)_2$	fluorescing green	

÷ Please read carefully the notes before proceeding with the identification of the cations:

Note	Comment
1	Fe^{2+} and Zn^{2+} both reacts selective with $K_3Fe(CN)_6$
2	Other cations that react with $K_4Fe(CN)_6$ to form highly colored precipitates must be absent (Co^{2+} and Fe^{3+} for example)
3	As is expected, when more than one cation from Fe^{3+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Al^{3+} is present in sample, the reaction with NH_4OH is not conclusive for the presence of any one
4	in the presence of both Fe^{3+} and Co^{2+} the identification of the Co^{2+} (blue) is possible with NH_4SCN in the presence of (by extracting it in) a mix of amyl alcohol and ether
5	Co^{2+} and Ni^{2+} both reacts selective with DMG(II)
6	When filter paper containing $Co(NO_3)_2$ and $Al_2(SO_4)_3$ is ignited produces an blue ash; reaction works in both senses, to identify Co (when $NaNO_3$ and HNO_3 is added on the filter paper and after migration of the $Co(NO_3)_2$ the $Al_2(SO_4)_3$ is added), and to identify Al (when Na_2SO_4 and H_2SO_4 is added on the filter paper and after migration of the $Al_2(SO_4)_3$ the $Co(NO_3)_2$ is added)
7	reaction works in both senses, to identify Co^{2+} (when $Zn(NO_3)_2$ is added), and to identify Zn^{2+} (when $Co(NO_3)_2$ is added)
8	forms a red complex soluble in organic solvents (such as benzene, toluene, etc)

÷ The substances from the reactions table have the chemical structural formulas and reacts as is given in the next table:

Name	Chemical formula	Complex
DMG		
Dipyridile		
sulphosalicylic acid		
Cuprone		
Cupferron		
Dithizone		
Alizarin		
Oxyne		

÷ Depending on the result of the identification (Yes/No) following table will be filled.

Sample	Cations→	Fe^{2+}	Fe^{3+}	Co^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cr^{3+}	Ni^{2+}	Al^{3+}
Name→										

Flame test

- When the previous reactions are not conclusive, can be proceeded further to see the color in the flame (by burning the filter paper with the sample of the metal ion on it);
- Following table contains the known color for the flame (thermal excitation) of the metallic cations:

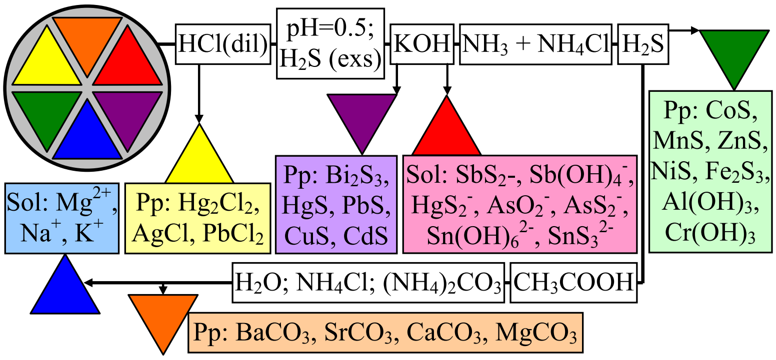
Ion	Flame color
Cr^{2+}	silver white
Cr^{3+}	violet (in the presence of NO_3^-)
Cr^{6+}	orange
Ni^{2+}	bluish-green
Mn^{2+}	pink
Pb^{2+}	light blue
Zn^{2+}	light green
Cu^{2+}	bluish-green
$Cu(NH_3)_4^{2+}$	dark blue
$FeSCN^{2+}$	red-brown (wine-red to dark-orange)
Al^{3+}	silver-white; in very hot flame light-blue
Na^+	yellow-orange
K^+	purple

Interpretation of the results

- The (previous) table will contain all the results obtained in a group of students;
- Each student labels its sample with its name;
- For its sample each student will write (again) the identification reactions (only) for the identified cations;
- For each written (again) reaction the coefficients (conserving the number of atoms for each species from reactants to products) must be established;
- To do at home: based on the (metals) content of the sample please use the literature (available on Internet for instance) to identify the name of the alloy (if available and if applies) from which the sample was taken (see also [[172]] and [[173]]).

Further reading

Actually the analysis of the cations requires (as is supposed to be observed from conducting the experiments) separation of them in smaller groups in order to avoid the interference of one to another in the identification process (see also [[174]]). This separation can be conducted on 'analytical groups' when based on their selectivity (to react and on the properties of the compounds) with a series of anions, the cations are divided in groups, as the following image shows:



Of course that the separation can continue and the general idea is to combine in the analysis chemical with instrumental methods (see also [131], [175], [176], [177] and [178]).

Study of chemical reactions

Introduction

In general, a chemical reaction may be defined as a process that leads to the transformation of one set of chemical substances (called reactants or reagents) to another (called products), in which the changes involve only the positions of electrons in the forming and breaking of chemical bonds between atoms (with no change to the nuclei).

A chemical process may involve more than a chemical reaction and then a chemical reaction is the transformation in which the participants (the reactants and the products) are known. For defined participants the chemical reactions are described with chemical equations, which graphically present the starting materials, end products, and sometimes intermediate products and reaction conditions. A chemical equation is written in general as "Reactants → Products", in which the "→" symbol express the creation of the reaction products ("Products") from the reactants ("Reactants"). A concept related to the chemical reaction concept is chemical equilibrium. Theoretically all chemical reactions evolves to an equilibrium between the reactants and the products but in some cases this equilibrium may be shifted to the left (to the reactants) or to the right (to the products), and it depends on a series of factors including temperature, pressure, environment (for instance catalysts) and the interaction of the system of reaction with it (the system of reaction may be 'open' meaning that is possible the transfer of the substance to and from environment, or may be 'closed', meaning that no transfer with the environment is allowed).

In a system is possible to move the chemical equilibrium if the transformation is accompanied by a transfer of substance (to and from environment). Thus, the $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$ reaction, with occurs at the contact surface between Zn (solid) and HCl solution (liquid) is a 'total' reaction if the released hydrogen leaves the system (for instance if the surface of the liquid is in contact with the atmosphere, where H_2 arrives, being thus send away from reaction environment). In these cases it may be considered that the reactions are total (the entire quantity of Zn or the entire quantity of HCl are consumed - whichever is the first).

A chemical reaction is named 'total' if the equilibrium is strongly shifted to the right, meaning that at the end of the reaction very little quantity (negligible) of reactants is still present in the system (of reaction). The applications of the total reactions include the chemical methods for determining the chemical composition, and are applied on large scale for reactions in aqueous environment. Total reactions may be found between:

÷ Acid-base reactions. An acid-base reaction involves a transfer of protons (H^+, H_3O^+) from one species (the acid) to another (the base). A special case of the acid-base reaction is the neutralization where an acid and a base, form a salt and water.

- ÷ Precipitation. Precipitation is the formation of a solid in a solution (or inside another solid) during a chemical reaction. It usually takes place when the concentration of dissolved ions exceeds the solubility limit and forms an insoluble salt. For some applications, see [179], [180].
- ÷ Complexation. In complexation reactions, several ligands (they can be both ions and neutral molecules, such as carbon monoxide, ammonia or water) react with one (or more) 'central' atom (usually a metallic one) to form a coordination complex (ligands surrounding the central atoms). This is achieved by providing lone pairs of the ligand into empty orbitals of the central atom(s) and forming dipolar bonds. Complexation reactions also include ligand exchange, in which one or more ligands are replaced by another, and redox processes (see also [181]) which change the oxidation state of the central atom(s).

An important task dealing with chemical total reactions is the establishing of the ratios between the participants. These ratios result by natural way, applying the conservation principles operating during reactions, which are translated in the chemical reaction equation as coefficients of the participants. For classical chemical reactions (not including here transformations at the level of the atoms nucleuses) when the electrical current is not involved is applied the ***principle of number of atoms (for each element) conservation*** which postulates that for each element (let be 'E' an element) the number of atoms (let be N('E',U) the number of E atoms in the U chemical compound) before (reaction) is equal with the number of atoms after (reaction).

For an reaction expressed as: $\Sigma_{1\leq i\leq m}\alpha_iR_i \rightarrow \Sigma_{1\leq j\leq n}\beta_jP_j$, in which $(\alpha_i)_{1\leq i\leq m}$ are the coefficients of the $(R_i)_{1\leq i\leq m}$ reactants and $(\beta_j)_{1\leq j\leq n}$ are the coefficients of the $(P_j)_{1\leq j\leq n}$ products, the principle of number of atoms conservation provides one equality relationship for each element: $\Sigma_{1\leq i\leq m}\alpha_i\cdot N('E',R_i) = \Sigma_{1\leq j\leq n}\beta_j\cdot N('E',P_j)$.

Turning back to aqueous environments, when conducting reactions in, an important point for the 'total' reactions is the equivalence point, defined as the moment, when (at least a part of the) reactants react wholly, when, based on the equation of the chemical reaction is possible to obtain the quantity of the reactants consumed when one of them is known (for instance by adding it in small quantities till the equivalence point is reached).

Considering thus the general reaction $\alpha_1R_1 + \Sigma_{2\leq i\leq m}\alpha_iR_i \rightarrow \Sigma_{1\leq j\leq n}\beta_jP_j$ when a known quantity (in number of molecules, or, more convenient, in number of moles) of the R_1 reactant, let's say a_1 (moles) is added in the reaction system till the moment when the equivalence point of the reaction is reached, then at least one of the other reactants (from R_2 to R_m) is completely consumed, and the quantities of the reactants which reacted to form the products are: $a_1\cdot\alpha_1/\alpha_1$, $a_1\cdot\alpha_2/\alpha_1$, …, $a_1\cdot\alpha_m/\alpha_1$ (in same units as a_1).

Of practical importance when conducting chemical reactions in aqueous solutions is expressing of the concentration on different scales, given in the next table ($L = dm^3$), because most of the chemical reactions occurs in aqueous phase (see [182], [183], [184], [185], [186] as examples);

Name	Formula	Quantities involved	Units
Mass concentration	$\rho_i = \frac{m_i}{V}$	ρ_i is the mass concentration of the constituent i m_i is the mass of the constituent i V is the volume of the mixture	$\frac{kg}{m^3} = \frac{g}{L}$
Molar concentration	$c_i = \frac{n_i}{V}$	c_i is the molar concentration of the constituent i n_i is the amount (in moles) of the constituent i V is the volume of the mixture	$\frac{mol}{m^3} = 10^{-3} \cdot \frac{mol}{L}$
Number concentration	$C_i = \frac{N_i}{V}$	C_i is the molar concentration of the constituent i N_i is the number of entities of the constituent i V is the volume of the mixture	$\frac{1}{m^3} = 10^{-3} \cdot \frac{1}{L}$
Volume concentration	$\phi_i = \frac{V_i}{V}$	ϕ_i is the volume concentration of the constituent i V_i is the volume of the constituent i V is the volume of the mixture	$1 = 100\%$
Normality	$\nu_i = \frac{c_i}{e_i}$	c_i is the molar concentration of the constituent i e_i is the number of reactive species of constituent i when dissolved (H^+, HO^-, e^-, nM^+)	$N = \frac{Eq}{L}$
Molality	$b_i = \frac{n_i}{m}$	b_i is the molality of the constituent i n_i is the amount (in moles) of the constituent i m is the mass of the mixture	$\frac{mol}{kg} = 10^{-3} \cdot \frac{mol}{g}$
Mole fraction	$x_i = \frac{n_i}{n}$	x_i is the mole fraction of the constituent i n_i is the amount (in moles) of the constituent i n is the amount (in moles) of the mixture ($n = \Sigma_j n_j$)	$1 = 100\%$
Mole ratio	$r_i = \frac{n_i}{n - n_i}$	r_i is the mole ratio of the constituent i n_i is the amount (in moles) of the constituent i n is the amount (in moles) of the mixture ($n = \Sigma_j n_j$)	$\frac{mol}{mol}$
Mass fraction	$w_i = \frac{m_i}{m}$	w_i is the mass fraction of the constituent i m_i is the mass of the constituent i m is the mass of the mixture	$1 = 100\%$
Mass ratio	$\varsigma_i = \frac{m_i}{m - m_i}$	ς_i is the mass ratio of the constituent i m_i is the mass of the constituent i m is the mass of the mixture	$\frac{kg}{kg} = \frac{g}{g} = 10^3 \cdot \frac{g}{kg}$
Titer (titre)	$T_i = \frac{m_i}{V}$	T_i is the titer of the constituent i m_i is the mass of the constituent i V is the volume of the mixture (aqueous solution)	$\frac{kg}{L} = \frac{g}{mL}$
Mass percent concentration	$\psi_i = 100 w_i$	ψ_i is the mass percent concentration of the constituent i w_i is the mass fraction of the constituent i	%
Volume percent concentration	$\Phi_i = 100 \phi_i$	ψ_i is the volume percent concentration of the constituent i ϕ_i is the volume concentration of the constituent i	%

Table 1. Concentration expressed in different units and having different references

Purpose

A series of three experiments will be conducted for quantitatively determination of the concentration of three solutions (NaOH, H_2SO_4 and $KMnO_4$). In order to do this a solution of known concentration will be used ($(COOH)_2$).

Material and method

When chemical reactions are used to obtain masses of the reactants, precautions must be taken with regard of the precision. Thus, not all chemicals are stable enough during time (in solid or in aqueous state) in order to be used as reference. To qualify as a reference, a reagent should have high purity, low reactivity (related to its stability), low hygroscopicity (humidity doesn't affect it too much), high equivalent height ($E_i = M_i/e_i$, minimizing weighting errors), as well as low toxicity and availability.

When is solved in water, oxalic acid (in solid state crystallizes with two water molecules, $(COOH)_2 \cdot 2H_2O$) can be used as analytical standard and therefore, by using a solution of an known concentration of oxalic acid can be obtained the corresponding quantity of other reactants which reacts with it. A typical application of the oxalic acid as reference is involving it in a reaction with a base, as following:

$$1(COOH)_2 + 2MOH \rightarrow 1(COOM)_2 + 2H_2O \text{ where M can be K or Na}$$

Potassium hydroxide (KOH) has many industrial and niche applications exploiting its reactivity toward acids and its corrosive nature. KOH is noteworthy as the precursor to most soft and liquid soaps as well as numerous potassium-containing chemicals. Potassium hydroxide is usually available as translucent pellets, which will become tacky in air because KOH is hygroscopic. Consequently, KOH typically contains varying amounts of water (as well as carbonates). For the preparation of the KOH solutions of known concentrations, the water stored in its solid state is an inconvenient which can be solved by determining its content (in KOH) by involving it in neutralization reactions (as the reaction with oxalic acid). About the same idea applies to sodium hydroxide (NaOH), being a caustic reagent that is widely used to neutralize acids and prepare sodium salts of reagents. It is also used in a variety of large scale applications, such as pulp and paper manufacturing, the manufacture of soap and detergents, and water treatment. These alkalis (KOH and NaOH) are deliquescent and readily absorb moisture and carbon dioxide in air.

Their solutions are with a reduced stability in air, due to formation of carbonate in solution ($KOH + CO_2 \rightarrow KHCO_3$; $KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O$; $NaOH + CO_2 \rightarrow NaHCO_3$; $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$). Due to the presence of the carbonate ions in solution, when KOH (or NaOH) solution is titred with an acid, its titration curve have two inflexion points, one corresponding to the total content of K^+ (or Na^+) ions and other one corresponding to the moving of the equilibrium $CO_2 + H_2O \rightarrow H_2CO_3$ to the formation of H_2CO_3. This is the reason for which the KOH and NaOH solutions are not considered analytical standards, and should be prepared with precautions (by expelling the carbon dioxide by boiling the solution or by purging it with an inert gas, [187]) determined immediately before its use in quantitative determinations.

Once determined the concentration of the base (MOH) this base can be further used to determine the concentration of an acid, as following:

$$2MOH + 1H_2SO_4 \rightarrow 1M_2SO_4 + 2H_2O \text{ or } 1MOH + 1HNO_3 \rightarrow 1MNO_3 + 1H_2O$$

Potassium permanganate ($KMnO_4$) may contain reduced products like manganese oxide MnO_2 where the concentration of $KMnO_4$ is changed after preparation because it dissociated via reducing agents such as ammonia and organic substances in water; therefore, potassium permanganate must be standardized before use it and keep it at least 7-10 days after preparation at dark place and in a dark bottle.

Using the following chemical reaction (when Mn^{7+} reduces to Mn^{2+} in excess of H_2SO_4) the concentration of the $KMnO_4$ solution can be determined:

$$2\mathrm{KMnO_4} + 5\mathrm{(COOH)_2} + 3\mathrm{H_2SO_4} \rightarrow 1\mathrm{K_2SO_4} + 2\mathrm{MnSO_4} + 8\mathrm{H_2O} + 10\mathrm{CO_2}$$

In order to express concentration in different units is necessary to relate the fundamental units given in Table 1. Thus, the mixture's mass (m) and mixture's volume (V) are related one to each other by using the mixture's density (ρ): $\rho = m/V$, as well as it exists the relationship between the number of moles (n_i) and the mass (m_i) when the molecular mass (M_i) is known: $n_i = m_i/M_i$. Going further, is necessary the expression of the density as a function of the concentration (see Table 2).

Solution	Variable	Function, f(x)
KOH in H_2O	$\rho = f(c)$	$10.19_{\pm0.70} - 4.41_{\pm0.31} \cdot \ln(x + 12.63_{\pm0.51}) + 0.654_{\pm0.039} \cdot (\ln(x + 5.75_{\pm0.48}))^2$
	$\rho = f(b)$	$(0.9979_{\pm0.0002} + 0.0917_{\pm0.0012} \cdot x)/(1 + 0.04285_{\pm0.0010} \cdot x - 3.72_{\pm1.44} \cdot 10^{-5} \cdot x^2)$
	$\rho = f(w)$	$1.256_{\pm0.052} - 0.257_{\pm0.052} \cdot \exp(+3.15_{\pm0.54} \cdot x) + 0.976_{\pm0.043} \cdot x^{1.703_{\pm0.066}}$
NaOH in H_2O	$\rho = f(c)$	$0.9982_{\pm0.0001} + 4.739_{\pm0.072} \cdot 10^{-2} \cdot x^{1.001_{\pm0.008}} - 4.479_{\pm0.083} \cdot 10^{-3} \cdot x^{1.51_{\pm0.03}}$
	$\rho = f(b)$	$1.636_{\pm0.001} - \frac{6.357_{\pm0.006} \cdot \exp(-x/14.79_{\pm0.03})}{10} - \frac{1.81_{\pm0.17} \cdot \exp(-x/3.15_{\pm0.54})}{1000}$
	$\rho = f(w)$	$0.9985_{\pm0.001} + \frac{x \cdot \exp(-1.571_{\pm0.167} \cdot x)}{0.9056_{\pm0.0035} - 1.408_{\pm0.117} \cdot x + 0.9535_{\pm0.1054} \cdot x^2}$
$KMnO_4$ in H_2O	$\rho = f(c)$	$0.9986_{\pm0.0002} + 0.1029_{\pm0.0008} \cdot x$
	$\rho = f(b)$	$0.9988_{\pm0.0003} + 0.1003_{\pm0.0014} \cdot x$
	$\rho = f(w)$	$0.9983_{\pm0.0001} + 0.6779_{\pm0.0016} \cdot x$
$H_2C_2O_4$ in H_2O	$\rho = f(c)$	$1.411_{\pm0.031} - 3.811_{\pm0.605} /(9.24_{\pm0.77} + x)$
	$\rho = f(b)$	$\frac{0.9981_{\pm0.0001} - 0.789_{\pm0.121} \cdot x - 0.213_{\pm0.018} \cdot x^2}{1 - 0.836_{\pm0.120} \cdot x - 0.168_{\pm0.019} \cdot x^2}$
	$\rho = f(w)$	$1.146_{\pm0.026} + 0.306_{\pm0.044} \cdot \ln(x + 0.616_{\pm0.095})$
H_2SO_4 in H_2O	$\rho = f(c)$	$0.9977_{\pm0.007} + \frac{x \cdot \exp(-0.1069_{\pm0.021} \cdot x)}{15.3_{\pm0.1} - 1.17_{\pm0.01} \cdot x + 2.75_{\pm0.04} \cdot 10^{-2} \cdot x^2}$
	$\rho = f(b)$	$1.796_{\pm0.019} - 0.111_{\pm0.028} \cdot \exp(-x/4.03_{\pm0.55}) - 0.687_{\pm0.010} \cdot \exp(-x/18.1_{\pm1.6})$
	$\rho = f(w)$	$1.835_{\pm0.003} + 0.511_{\pm0.008} \cdot x - \arctan(0.461_{0.006} /(x - 0.823_{\pm0.013}))/\pi$
HNO_3 in H_2O	$\rho = f(c)$	$1.276_{\pm0.005} + 2.382_{\pm0.043} \cdot 10^{-2} \cdot \lvert 9.14_{\pm0.2} - x \rvert^{1.111_{\pm0.005}}$
	$\rho = f(b)$	$0.9982_{\pm0.0001} + 3.453_{\pm0.019} \cdot 10^{-2} \cdot x^{1.005_{\pm0.007}} - 1.82_{\pm0.27} \cdot 10^{-3} \cdot x^{1.78_{\pm0.03}}$
	$\rho = f(w)$	$0.9982_{\pm0.001} + \frac{x \cdot \exp(-1.473_{\pm0.083} \cdot x)}{1.852_{\pm0.005} - 3.362_{\pm0.109} \cdot x + 2.416_{\pm0.113} \cdot x^2}$
$CuSO_4$ in H_2O	$\rho = f(c)$	$0.9981_{\pm0.0001} - 1.653_{\pm0.007} \cdot 10^{-1} \cdot x - 1.512_{\pm0.133} \cdot 10^{-2} \cdot x^2 + 4.361_{\pm0.651} \cdot 10^{-3} \cdot x^3$
	$\rho = f(b)$	$\frac{0.9981_{\pm0.0001} + 0.3726_{\pm0.038} \cdot x}{1 + 0.2075_{\pm0.037} \cdot x - 1.725_{\pm0.419} \cdot 10^{-2} \cdot x^2}$
	$\rho = f(w)$	$1.922_{\pm0.009} + 0.865_{\pm0.017} \cdot x - \arctan(0.102_{0.016} /(x - 0.419_{\pm0.012}))/\pi$

Table 2. Density as a function of temperature for some aqueous solutions at 20°C

When is necessary the expression of the density as a function of the experimental conditions - pressure, temperature, and concentration (if applies) then following equations can be used:

- for water density (g/cm^3) as function of pressure ($p \in [0.8, 1.2]$ atm) and temperature ($t \in [0, 90]$ °C) following equation can be used:

$$\rho = \frac{0.99973_{\pm 0.0001\%} + 0.01334_{\pm 0.2\%} \cdot t - 8.0874_{\pm 0.04\%} \cdot 10^{-6} \cdot t^2 - 2.258_{\pm 0.3\%} \cdot 10^{-8} \cdot t^3 + 1.5_{\pm 5\%} \cdot 10^{-3} \cdot p}{1 + 1.327_{\pm 0.2\%} \cdot 10^{-2} \cdot t + 1.445_{\pm 5\%} \cdot p}$$

- for NaOH density (g/cm^3) as a function of temperature ($t \in [0, 100]$ °C) and concentration ($c \in [0, 0.5] \cdot 100\%_{wt}$) following equation can be used:

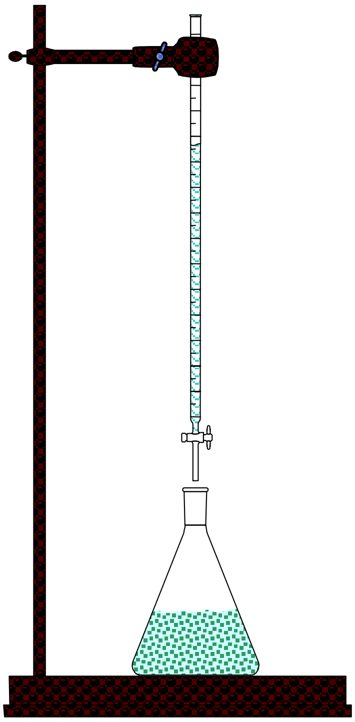
$$\rho = \frac{1.006_{\pm 0.001} + 1.296_{\pm 0.029} \cdot c - 4.537_{\pm 0.201} \cdot 10^{-4} \cdot t}{1 + 1.432_{\pm 0.194} \cdot 10^{-1} \cdot c + 4.849_{\pm 0.517} \cdot c \cdot t}$$

- for H_2SO_4 density (g/cm^3) as a function of temperature ($t \in [0, 50]$ °C) and concentration ($c \in [0.1, 0.9] \cdot 100\%_{wt}$) following equation can be used:

$$\rho = \frac{0.9561_{\pm 0.007} + 0.4869_{\pm 0.0038} \cdot c - 1.3777_{\pm 0.0048} \cdot \sqrt{c} - 3.696_{\pm 0.040} \cdot 10^{-4} \cdot t - 3.402_{\pm 0.068} \cdot 10^{-4} \cdot t \cdot \sqrt{c}}{1 + 0.7635_{\pm 0.0036} \cdot c - 1.7283_{\pm 0.0063} \cdot \sqrt{c}}$$

When chemical reactions are conducted to obtain the equivalent quantity of a reagent, useful are the substances called 'indicators' which in very small quantities changes their colour in a certain pH range. Following table contain a list of the indicators, along with the pair of colours and the corresponding pH range for the shift:

Indicator	Color low	Range	Color high	color low	color high
Picric acid	⬜	0.6-1.3	🟨	transparent	yellow
Thymol 'blue'	🟥	0.6-1.3	🟨	red	yellow
2,4-dinitrophenol	⬜	0.6-1.3	🟨	transparent	yellow
Methyl 'yellow'	🟥	2.9-4.0	🟨	red	yellow
Bromophenol 'blue'	🟨	3.0-4.6	🟪	yellow	violet
Congo 'red'	🟪	3.0-5.0	🟥	indigo	red
Methyl 'orange'	🟥	3.1-4.4	🟨	red	yellow
Bromocresol 'green'	🟨	3.8-5.4	🟦	yellow	blue
Methyl 'red'	🟥	4.3-6.2	🟨	red	yellow
Azolitmin	🟥	4.5-8.3	🟦	red	blue
Bromocresol 'purple'	🟨	5.2-6.8	🟪	yellow	purple
Bromothymol 'blue'	🟨	6.2-7.6	🟦	yellow	blue
Phenol 'red'	🟨	6.4-8.0	🟥	yellow	red
Toluylene 'red'	🟥	6.8-8.0	🟨	red	yellow
Cresol 'red'	🟨	7.2-8.8	🟥	yellow	pink
Naphtholphthalein 'blue'	🟪	7.3-8.7	🟦	pale violet	turquoise
Thymol 'blue'	🟨	8.0-9.6	🟦	yellow	blue
Phenolphthalein	⬜	8.3-10.0	🟪	transparent	fuchsia
Thymolphthalein	⬜	8.3-10.0	🟦	transparent	blue
Alizarine 'yellow'	🟨	10.1-12.0	🟥	yellow	red
Picrylnitromethylamine	⬜	10.8-13.0	🟫	transparent	brown
Cyanidin	<3.0	7.0-8.0	>11	pale violet	sky blue



Burette for titration

Table 3. Indicators to be used to signal the equivalence point in the titration reactions

Usually titrations are conducted adding distilled water in the flask such that at the beginning of the titration to have the flask of about 1/3 full with reactive (see burette in Table 3).

Working procedure

For titration of NaOH with $H_2C_2O_4$ the succession of the steps is as follows:

- Three samples of NaOH of known volumes (of about 5 ml, measured with the burette) are taken in (three) Erlenmeyer flask(s), the results being recorded in Table 4. For each one out of three samples:
    - The initial volume in the burette containing NaOH is recorded ($V_{initial}$ column in Table 4);
    - The burette is used to take the approximate volume of NaOH given above;
    - The final volume in the burette containing NaOH is recorded (V_{final} column in Table 4);
    - One drop of indicator (usually the indicator is phenolphthalein) is added (to provide the change of the colour of the solution when the equivalence point is passed); is added distilled water;
- By using the solution of oxalic acid (from the burette containing it) the titration of the sodium hydroxide is conducted for each of the three samples, the results being recorded in Table 4. For each one out of three samples:
    - The initial volume in the burette containing $H_2C_2O_4$ is recorded ($V_{initial}$ column in Table 4);
    - The reaction between NaOH and $H_2C_2O_4$ is conducted till the moment in which the indicator indicate the equilibrium point (change in the colour of the solution);
    - The final volume in the burette containing $H_2C_2O_4$ is recorded (V_{final} column in Table 4);
- The differences between initial and final volumes (ΔV), their ratio as well as the average between samples are calculated and recorded in Table 4.

$1(COOH)_2 + 2NaOH \rightarrow 1(COONa)_2 + 2H_2O$								
	NaOH (ml)			$H_2C_2O_4$ (ml)			$\frac{\Delta V(H_2C_2O_4)}{\Delta V(NaOH)}$	$a_1 = \text{Average}\left(\frac{\Delta V(H_2C_2O_4)}{\Delta V(NaOH)}\right)$
Sample	$V_{initial}$	V_{final}	ΔV	$V_{initial}$	V_{final}	ΔV		
1								$a_1 =$
2								
3								

Table 4. Experimental data for titration of NaOH with $H_2C_2O_4$

For titration of H_2SO_4 with NaOH the succession of the steps is as follows:

- Three samples of H_2SO_4 of known volumes (of about 5 ml, measured with the burette) are taken in (three) Erlenmeyer flask(s), the results being recorded in Table 5. For each one out of three samples:
    - The initial volume in the burette containing H_2SO_4 is recorded ($V_{initial}$ column in Table 5);
    - The burette is used to take the approximate volume of H_2SO_4 given above;
    - The final volume in the burette containing H_2SO_4 is recorded (V_{final} column in Table 5);
    - One drop of indicator (usually the indicator is phenolphthalein) is added (to provide the change

of the colour of the solution when the equivalence point is passed); is added distilled water;

- By using the solution of sodium hydroxide (from the burette containing it) the titration of the sulphuric acid is conducted for each of the three samples, the results being recorded in Table 5. For each one out of three samples:
    - The initial volume in the burette containing NaOH is recorded ($V_{initial}$ column in Table 5);
    - The reaction between H_2SO_4 and NaOH is conducted till the moment in which the indicator indicate the equilibrium point (change in the colour of the solution);
    - The final volume in the burette containing NaOH is recorded (V_{final} column in Table 5);
- The differences between initial and final volumes (ΔV), their ratio as well as the average between samples are calculated and recorded in Table 5.

$2NaOH + 1H_2SO_4 \rightarrow 1Na_2SO_4 + 2H_2O$								
	H_2SO_4 (ml)			NaOH (ml)			$\frac{\Delta V(NaOH)}{\Delta V(H_2SO_4)}$	$a_2 = \text{Average}\left(\frac{\Delta V(NaOH)}{\Delta V(H_2SO_4)}\right)$
Sample	$V_{initial}$	V_{final}	ΔV	$V_{initial}$	V_{final}	ΔV		
1								a_2 =
2								
3								

Table 5. Experimental data for titration of H_2SO_4 with NaOH

As preliminary for titration of $(COOH)_2$ and H_2SO_4 with $KMnO_4$ a calculation is conducted. Known volumes (of about x = 5 ml, measured with the burette) of $(COOH)_2$ will be taken (using the burette). Enough (to be corresponding) quantities of H_2SO_4 will be added (using the burette). The corresponding quantity of H_2SO_4 is calculated from the equivalence with $(COOH)_2$ and is $y = (3/5)\cdot x/(a_1\cdot a_2)$ ml, where a_1 is from Table 4, a_2 is from Table 5, x is the quantity of $(COOH)_2$. The values are to be written in Table 6.

$a_1\cdot a_2$ =	$(COOH)_2$ solution	H_2SO_4 solution
Volume (in ml)	x =	y =

Table 6. Equivalence between $(COOH)_2$ and H_2SO_4 to be used for titration of $KMnO_4$

In three Erlenmeyer flasks, the succession of the steps is as follows (repeated for each flask):

- Sample of x (ml) as approximate volume of $(COOH)_2$ is taken into (recording initial volume, final volume and their difference in Table 7);
- An approximate volume of y + 1 (ml) of H_2SO_4 is added (recording initial volume, final volume and their difference in Table 7);
- The flask is warmed up using a gas burner; the reaction requires heat in order to proceed fast; about 60° C are enough; from this point on with the heated flask the titration with $KMnO_4$ is conducted manipulating the flask with a paper sleeve:
    - The initial volume in the burette containing $KMnO_4$ is recorded ($V_{initial}$ column in Table 7);
    - The reaction of between $KMnO_4$ (from burette) with the mixture of H_2SO_4 and $H_2C_2O_4$ (from flask) is conducted till the moment in which the colour of the mixture in the flask become the

same with the colour of the $KMnO_4$ (pink or purple), indicating that the equivalence point has been reached;

  - The final volume in the burette containing $KMnO_4$ is recorded (V_{final} column in Table 7);
- The differences between initial and final volumes (ΔV), their ratio as well as the average between samples are calculated and recorded in Table 7.

$2KMnO_4 + 5(COOH)_2 + 3H_2SO_4 \rightarrow 1K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$											
	$(COOH)_2$			H_2SO_4			$KMnO_4$			$\frac{\Delta V(KMnO_4)}{\Delta V(H_2C_2O_4)}$	$a_3 = \text{Average}\left(\frac{\Delta V(KMnO_4)}{\Delta V(H_2C_2O_4)}\right)$
Sample	$V_{initial}$	V_{final}	ΔV	$V_{initial}$	V_{final}	ΔV	$V_{initial}$	V_{final}	ΔV		
1											$a_3 =$
2											
3											

Table 7. Experimental data for titration of H_2SO_4 and $H_2C_2O_4$ with $KMnO_4$

Data analysis

The concentrations of the solutions are expressed in different units and using different references by filling the next table (Table 8). In order to do this, are used:

- Concentration of $H_2C_2O_4$ solution, from the reagent bottle (along with its measurement units!);
- The values from the experiments (a_1 from Table 4, a_2 from Table 5, a_3 from Table 7);
- Formulas expressing different concentrations from Table 1;
- Density (ρ) as a function of concentration from Table 2;

Name, units and formula	$H_2C_2O_4$	NaOH	H_2SO_4	$KMnO_4$
Exchanged electrons, e_i =	2	1	2	5
Molecular mass (g/mol), M_i =	90.03	40.00	98.08	158.03
Volume used, $(\Delta V_{Sample1} + \Delta V_{Sample2} + \Delta V_{Sample3})/3$ =				
Mass concentration (g/L), $\rho_i = m_i/V$ =				
Molar concentration (mol/L), $c_i = n_i/V$ =				
Volume concentration (adimensional), $\phi_i = V_i/V$ =				
Normality (Eq/L), $\nu_i = c_i/e_i$ =				
Molality (mol/g), $b_i = n_i/m$ =				
Mole fraction (adimensional), $x_i = n_i/n$ =				
Mole ratio (mol/mol), $r_i = n_i/(n-n_i)$ =				
Mass fraction (adimensional), $w_i = m_i/m$ =				
Mass ratio (g/g), $\varsigma_i = m_i/(m-m_i)$ =				
Titre (g/mL), $T_i = m_i/V$ =				
Mass percent concentration (%),$\Psi_i = 100 \cdot w_i$ =				
Volume percent concentration (%),$\Phi_i = 100 \cdot \phi_i$ =				
Solution's density (kg/m^3) from its concentration, ρ =				
Solution's mass (kg) $m = V \cdot \rho$ =				

Table 8. Concentrations of the solutions, expressed in different units and having different references

Hints to fill the Table 8:

- Start with the filling of the concentration of $H_2C_2O_4$ given on the reagent bottle (in its proper place taking into consideration its measurement units);

- Calculate the density of $H_2C_2O_4$ from its concentration (using the proper formula given in Table 2);
- Calculate the average of the $H_2C_2O_4$ volume used (here are actually three 'average volumes' used, one for each reaction; here is about first one, $1(COOH)_2 + 2NaOH \rightarrow 1(COONa)_2 + 2H_2O$), $V(H_2C_2O_4) = (\Delta V_{Sample1}(H_2C_2O_4) + \Delta V_{Sample2}(H_2C_2O_4) + \Delta V_{Sample3}(H_2C_2O_4))/3$; with the density immediately results its mass, $m = V\cdot\rho$;
- By using the other given values (molar masses, exchanged electrons), its only a mater of substitutions with values in the formulas to obtain all other concentrations;
- The key point to pass from one column to another (from first to second being given here) is to express the molar concentration $c(H_2C_2O_4)$, if this concentration is not the one given on the reagent bottle; then, the number of moles is $n(H_2C_2O_4) = c(H_2C_2O_4)\cdot V(H_2C_2O_4)$;
- Using the balanced chemical reaction calculate the number of moles of the others, as given below:

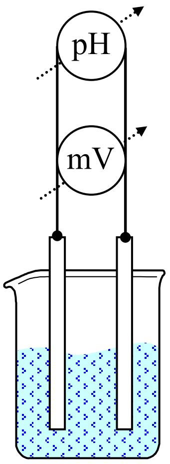
Equation of the chemical reaction	Moles correspondence
$1(COOH)_2 + 2NaOH \rightarrow 1(COONa)_2 + 2H_2O$	$n(NaOH) = 2\cdot n(H_2C_2O_4)$
$2NaOH + 1H_2SO_4 \rightarrow 1Na_2SO_4 + 2H_2O$	$n(H_2SO_4) = ½\cdot n(NaOH)$
$2KMnO_4 + 5(COOH)_2 + 3H_2SO_4 \rightarrow 1K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$	$n(KMnO_4) = {}^5/_2\cdot n(H_2C_2O_4)$

- Calculate the average of the volumes used in each reaction, $V(\cdot) = (\Delta V_{Sample1}(\cdot) + \Delta V_{Sample2}(\cdot) + \Delta V_{Sample3}(\cdot))/3$, for all reactants (here the volume of $H_2C_2O_4$ is subject to change from one reaction to another and should be considered the volume of $H_2C_2O_4$ implied in that reaction from which the corresponding quantity of another reactant is calculated);
- Using these volumes and the number of moles calculate the molar concentrations ($c = n/V$);
- Using the molar concentrations, calculates the densities (using appropriate formulas from Table 2);
- With the density immediately results the masses, $m(\cdot) = V(\cdot)\cdot\rho(\cdot)$;
- By using the other given values (molar masses, exchanged electrons), it's only a mater of substitutions with values in the formulas to obtain all other concentrations.

Further reading

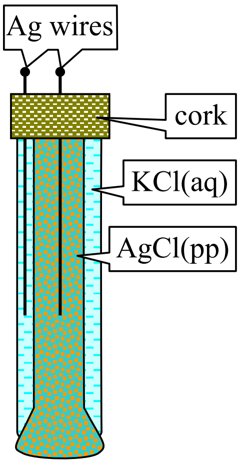
Potassium permanganate solution can be further used to oxidize organics, such as sugars (glucose, dextrose, lactose, galactose and fructose) in alkali (+ NaOH) or acid (+ H_2SO_4) environments. Unfortunately these reactions cannot be used to quantitatively determine the sugar content due to many pathways of evolution and formation of the numerous products ([188]). Other ways to oxidize sugars are changing the oxidation state of copper ions, by using some specific reagents, such as Fehling's reagent ([189]).

A stoechiometric neutralization reaction implies the passing from an acidic solution to a basic one (assuming that an acid is titrated with a basis; or vice-versa in the other way around) the evolution of the reaction can be traced determining the pH of the solution in a continuously way depending then on the quantity of the added solution. The common way is to use a device which converts the concentration of the hydrogen ions into electrical current in a small cell called electrochemical cell like the one depicted below (see also [190]). Actually, reference 'electrode' consists from a pair of electrodes, with a communicating membrane from which one is to be immersed in the solution to be measured (see the picture below).



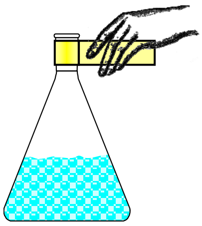
$$\mathrm{pH} = -\frac{E(H^+/H_2) + E_{ref} - E^0{}_{ref}}{\ln(10)\cdot RT/F}$$

Generic construction of an electrochemical cell



$E = E^0 - (RT/F)\cdot\ln(a(Cl-))$;
a = chemical activity;
$a = j\cdot c$; j = ionic strength

Constructive principle of an electrode



Manipulating the heated flask with a paper sleeve

A graphical representation of the pH (or of the potential, E) depending on the added quantity is called titration curve. By taking a titration curve, is possibly further to obtain (with a higher precision than the precision obtained using colour-based indicators) the volume which was necessary to neutralize the sample (for further details see [191], [192] and [193]).

To exemplify, let's take a weak acid (such as CH_3COOH = AcOH, $K_a(AcOH) = 1.76\cdot10^{-5}$) with a given concentration (C_a) to be titred with a weak base (such as NH_4OH, $K_b = 1.79\cdot10^{-5}$) with a given concentration (C_b). Along with the general equation of the reaction also the other (equilibrium) reactions must be considered, including water dissociation (H_2O, $K_w = 10^{-14}$):

$$HA + BOH \rightleftharpoons AB + H_2O$$

$$HOH \rightleftharpoons HO^- + H^+,\ [H^+]\cdot[HO^-] = K_w$$

$$HA \rightleftharpoons H^+ + A^-,\ [H^+]\cdot[A^-] = K_a\cdot[HA]$$

$$BOH \rightleftharpoons B^+ + HO^-,\ [HO^-]\cdot[B^+] = K_b\cdot[BOH]$$

$$AB \rightleftharpoons A^- + B^+,\ [A^-]\cdot[B^+] = K_s\cdot[AB]$$

For a number of n drops of the base (each drop having a volume V_b) over the solution of the acid (of a volume V_a) the total volume of water is $V_w = (1-C_a)\cdot V_a+(1-C_b)\cdot V_x$. Applying the conservation principle, $C_a = [HA] + [H^+] - [HO^-]$ and $C_s = [A^-] - [H^+] + [HO^-]$, leading us to a third degree equation in the Hydrons ($x = [H^+]$), where $C_s = C_b\cdot V_x/(V_a + V_x)$ and $C_x = (C_a\cdot V_a - C_b\cdot V_x)/(V_a+V_x)$: $x^3 + (K_a + C_s)\cdot x^2 - (K_w + C_x\cdot K_a)\cdot x - K_w\cdot K_a = 0$.

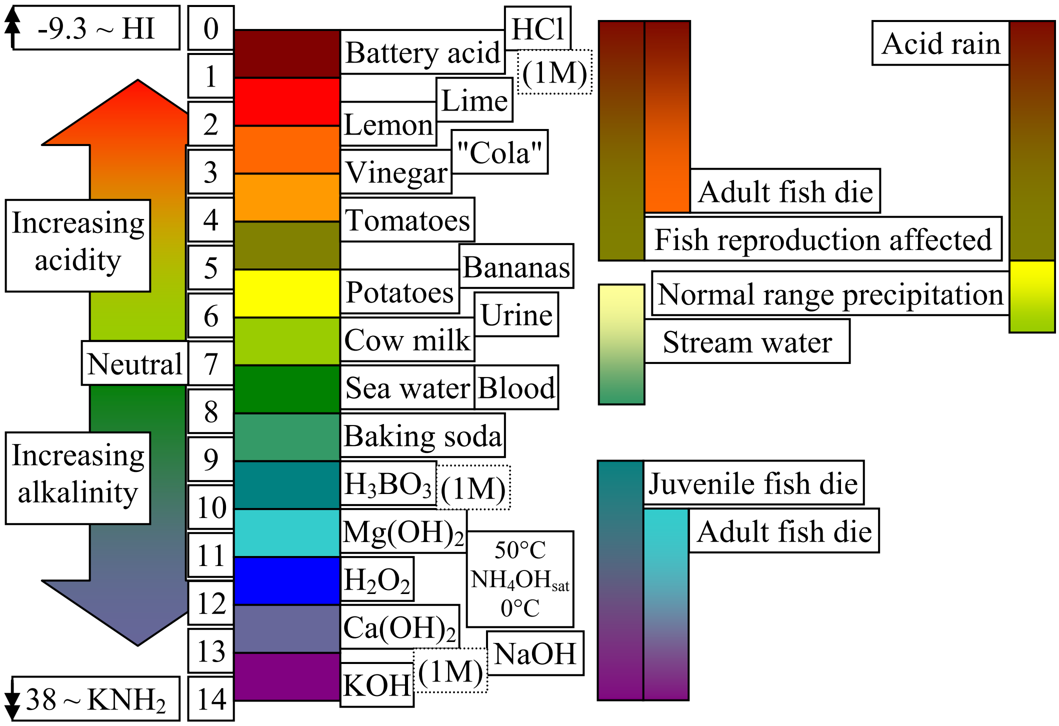
At equivalence point it exists a weak hydrolysis, and therefore then $C_s = [B^+] = [A^-]$ and

$$x^2 = (K_w \cdot K_a / K_b) \cdot (K_b + C_s)/(K_a + C_s)\text{, at equivalence point}$$

Analogues, $x^3 + (K_w/K_b + C_x)\cdot x^2 - (K_w + C_s\cdot K_w/K_b)\cdot x - K_w^2/K_b = 0$, when the equilibrium point is passed, where the expressions of C_x (base excess) and C_s are $C_x = (C_b\cdot V_x - C_a\cdot V_a)/(V_a + V_x)$ and $C_s = C_a\cdot V_a/(V_a+V_x)$. The third degree equations can be solved and their roots (only one having a true meaning, ranging in [0,1]) can be depicted as a function of the added volume. An online application implementing this procedure of calculation is available (see [194] and papers [195] and [196]).

Other sensor-based applications include [197], [198], [199], [200], [201], [202] and [203] (see also [204]).

The pH measurements (see [205], [206]; and in general, sensor based measurements, see for instance [207]) have very important applications, ranging from environmental and biological ones to industrial. An illustrative image about the pH of some common chemicals as well as natural products is given in the next:



Useful is also creation of a database (for fast procedures, see [208]) with equilibrium constants of chemical reactions (see [209] and [210]).

Water analysis

Introduction

In its liquid state, water forms the world's streams, rivers, lakes, oceans and rain and is the major constituent of the fluids of living things, its percent in the human body ranging from 50% to 80%.

Water is a good polar solvent (often referred as the universal solvent) dissolving more substances in greater quantities than any other common liquid being important in chemical, physical, and biological processes.

Sources of water include fresh water (from streams), salt water (from rivers and lakes), seawater (from seas and oceans) as well as icebergs (in the polar region) and glaciers (at upper altitudes in mountains).

Pure water (H_2O) essentially is nonexistent in the natural environment. Natural water, whether in the atmosphere, on the ground surface, or under the ground, always contains dissolved minerals and gases as a result of its interaction with the atmosphere, minerals in rocks, organic matter, and living organisms. Some of the substances are miscible (mix in all proportions), others are hydrophilic (that is attracted to and tends to be dissolved by water), others are soluble (depends on temperature, pressure and the pH) while others are immiscible (incapable of mixing or attaining homogeneity).

Water purification is the process of removing undesirable chemicals, biological contaminants, suspended solids and gases (for further details see [[211]], [[212]]). The goal of this process is to produce water fit for a specific purpose. Most water is disinfected for human consumption (drinking water) but water purification may also be designed for a variety of other purposes (meeting the requirements of medical [[213]], pharmacological [[214]], chemical and industrial [[215]] applications). Purification includes physical processes (filtration, sedimentation, and distillation), biological processes (using of slow sand filters and biologically active carbon), chemical processes (flocculation and chlorination).

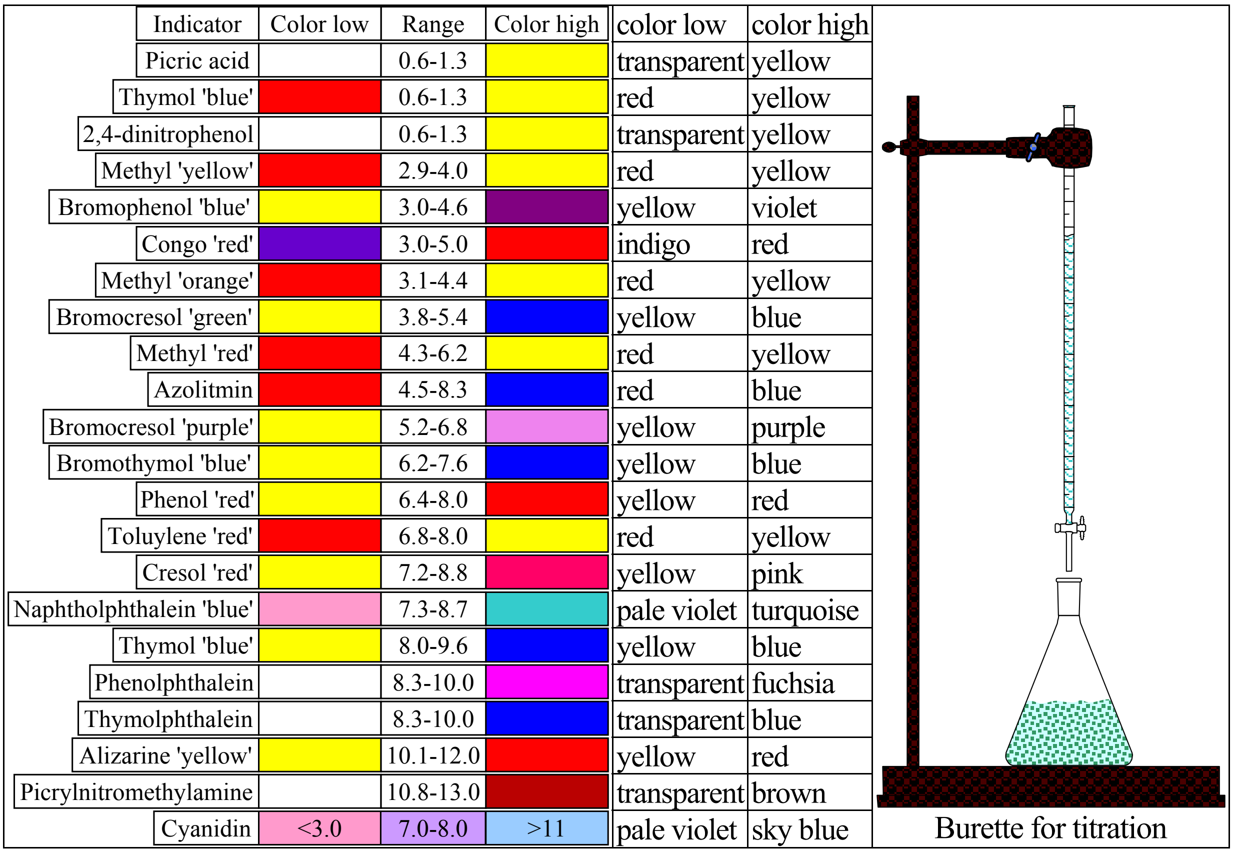
Water chemistry analyses are carried out to identify and quantify the chemical components and properties including pH, major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}) and anions (Cl^-, F^-, SO_4^{2-},NO_3^-), trace elements (Rb^+, Ti^{4+}, Fe^{2+}, Mn^{2+}, etc.), unstable volatiles (CO_2, H_2S, O_2) and isotopes (${}^{18}O^{2-}$, ${}^{2}H^+$), organics and nutrients.

Purpose

It will be determined acidity, alkalinity and total hardness of the water.

Material and method

Samples of water will be analyzed in the laboratory and a bulletin of water analysis will be obtained. In order to do this, samples of water will be taken from the tap and neutralization reactions will be conducted in order to quantify the water acidity and the water alkalinity, by using the burette and using colour indicators for the equivalence point of the reactions (see Figure 1).



Indicator	Color low	Range	Color high	color low	color high
Picric acid		0.6-1.3	🟨	transparent	yellow
Thymol 'blue'	🟥	0.6-1.3	🟨	red	yellow
2,4-dinitrophenol		0.6-1.3	🟨	transparent	yellow
Methyl 'yellow'	🟥	2.9-4.0	🟨	red	yellow
Bromophenol 'blue'	🟨	3.0-4.6	🟪	yellow	violet
Congo 'red'	🟪	3.0-5.0	🟥	indigo	red
Methyl 'orange'	🟥	3.1-4.4	🟨	red	yellow
Bromocresol 'green'	🟨	3.8-5.4	🟦	yellow	blue
Methyl 'red'	🟥	4.3-6.2	🟨	red	yellow
Azolitmin	🟥	4.5-8.3	🟦	red	blue
Bromocresol 'purple'	🟨	5.2-6.8	🟪	yellow	purple
Bromothymol 'blue'	🟨	6.2-7.6	🟦	yellow	blue
Phenol 'red'	🟨	6.4-8.0	🟥	yellow	red
Toluylene 'red'	🟥	6.8-8.0	🟨	red	yellow
Cresol 'red'	🟨	7.2-8.8	🟥	yellow	pink
Naphtholphthalein 'blue'	🟪	7.3-8.7	🟦	pale violet	turquoise
Thymol 'blue'	🟨	8.0-9.6	🟦	yellow	blue
Phenolphthalein		8.3-10.0	🟪	transparent	fuchsia
Thymolphthalein		8.3-10.0	🟦	transparent	blue
Alizarine 'yellow'	🟨	10.1-12.0	🟥	yellow	red
Picrylnitromethylamine		10.8-13.0	🟫	transparent	brown
Cyanidin	<3.0	7.0-8.0	>11	pale violet	sky blue

Figure 1. Indicators to be used to signal the equivalence point in the titration reactions

Tap water have dissociated in a series of salts, an as result, contains a series of ions (sum of all positive charges provided by cations is equal to sum of all negative charges provided by anions).

Cations	Anions
H^+, K^+, Ca^{2+}, Na^+, Mg^{2+}, $Others^+$	HO^-, $H_xCO_3^{(2-x)-}$, $H_xPO_4^{(3-x)-}$, $H_xSiO_3^{(2-x)-}$, SO_4^{2-}, Cl^-, NO_3^-, CH_3COO^-, $HCOO^-$, $Others^-$

Figure 2. Drinking water qualitative content

Water acidity is the quantitative expression of its capacity to neutralize a strong base to a designated pH being an indicator of how corrosive water is. Acidity can be caused by carbon dioxide (in the form of carbonic acid), weak organic acids (examples include acetic, citric, tannic and formic acids), and strong mineral acids (examples include sulphuric and chlorhydric acids). Acidity is determined by titration with sodium hydroxide (NaOH). Acidity determined in the presence of methyl orange (end point at pH of 3.7) corresponds to neutralization of the mineral acids, being named mineral acidity, while the acidity determined in the presence of phenolphthalein (end point at pH of 8.3) corresponds to the neutralization of carbonic acid to bicarbonate being named total acidity.

Water alkalinity is the quantitative expression of its capacity to neutralize a strong acid to a designated pH being an indicator of how much content in salts with basic hydrolysis have. Alkalinity can be caused by bicarbonates (HCO_3^-), carbonates (CO_3^{2-}), hydroxides (HO^-), and possibly to phosphates ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) and silicates ($HSiO_3^-$, SiO_3^{2-}). Alkalinity is determined by titration with chlorhydric acid (HCl). Alkalinity determined in the presence of phenolphthalein (end point at pH of 8.3) correspond to $[HO^-] + \frac{1}{2}[CO_3^{2-}] + {}^{1}/_{3}[PO_4^{3-}]$ being named partial alkalinity, while the alkalinity determined in the presence of methyl orange (end point at pH of 3.7) correspond to $[HO^-] + [CO_3^{2-}] + {}^{2}/_{3}[PO_4^{3-}]$, being named total alkalinity.

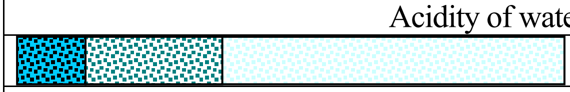
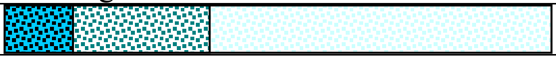
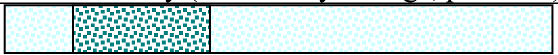
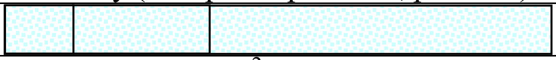
Acidity of water containing anions	
	
Water containing anions + NaOH Mineral acidity (with methyl orange, pH ~ 3.7)	Water containing anions + NaOH Total acidity (with phenolphthalein, pH ~ 8.3)
	
From strong acids (SO_4^{2-}, Cl^-, NO_3^-, etc.) $2NaOH + SO_4^{2-} \rightarrow Na_2SO_4 + 2HO^-$ $NaOH + Cl^- \rightarrow NaCl + HO^-$ $NaOH + NO_3^- \rightarrow NaNO_3 + HO^-$	From weak acids (CO_3^{2-}, CH_3COO^-, $HCOO^-$, etc.) $NaOH + CO_3^{2-} \rightarrow NaHCO_3^- + HO^-$ $NaOH + CH_3COO^- \rightarrow CH_3COONa + HO^-$ $NaOH + HCOO^- \rightarrow HCOONa + HO^-$
mineral	total = mineral + weak
Results of are reported in mg $CaCO_3$/L units: Acidity = $50000 \cdot V_{NaOH} \cdot c_{NaOH}/V_{sample}$	

Table 2. Water acidity measures

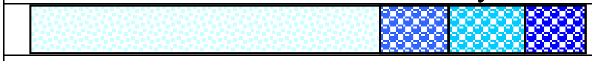
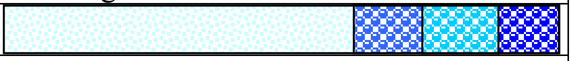
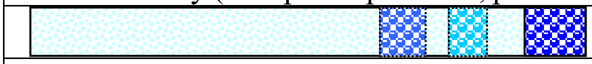
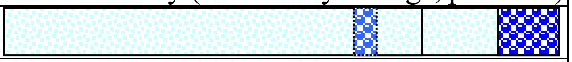
Alkalinity of water containing anions	
	
Water containing anions + HCl Partial alkalinity (with phenolphthalein, pH ~ 8.3)	Water containing anions + HCl Total alkalinity (with methyl orange, pH ~ 3.7)
	
$HCl + HO^- \rightarrow H_2O + Cl^-$ $HCl + CO_3^{2-} \rightarrow HCO_3^- + Cl^-$ $HCl + PO_4^{3-} \rightarrow HPO_4^{2-} + Cl^-$	$HCl + HO^- \rightarrow H_2O + Cl^-$ $2HCl + CO_3^{2-} \rightarrow H_2CO_3 + 2Cl^-$ $2HCl + PO_4^{3-} \rightarrow H_2PO_4^- + 2Cl^-$
partial alkalinity = $[HO^-] + \frac{1}{2}[CO_3^{2-}] + {}^{1}/_{3}[PO_4^{3-}]$	total alkalinity = $[HO^-] + [CO_3^{2-}] + {}^{2}/_{3}[PO_4^{3-}]$
Results of are reported in mg $CaCO_3$/L units: Alkalinity = $50000 \cdot V_{HCl} \cdot c_{HCl}/V_{sample}$	

Table 3. Water alkalinity measures

$M(CaCO_3)$ = 100g/mole and exchanges two e^-, and then it has 50 g/equivalent or 50000 mg/equivalent and thus the factor of 50000 is used to express in terms of mg $CaCO_3$/L.

Hardness of the water is due to the presence of Ca^{2+} and Mg^{2+}. The preferred method for determining hardness is to compute it from the results of separate determinations of the content in calcium ($[Ca^{2+}]$ in mg/L) and magnesium ($[Mg^{2+}]$ in mg/L), when the value of the hardness (in mg equivalent $CaCO_3$/L) = $2.497 \cdot [Ca^{2+}]_{mg/L} + 4.118 \cdot [Mg^{2+}]_{mg/L}$.

The alternative (see [216]) is the EDTA titrimetric method. Ethylenediaminetetraacetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of bivalent ions (M^{2+}, such as Ca^{2+}, Mg^{2+}, Fe^{2+}). If a small amount of a dye such as eriochrome black T is added to an aqueous solution containing Ca^{2+} and Mg^{2+} at a pH ~ 10.0 ± 0.1, the solution becomes wine red. If the solution is titred with EDTA, Ca^{2+} and Mg^{2+} will be complexed by EDTA, and when all of the M^{2+} are complexed, solution turning from wine red to blue, marking the end point of the titration. EDTA selectively complexes heavy metals too, and therefore, a small amount of neutral magnesium salt of EDTA is added to the buffer (introduces Mg^{2+} in solution, being released from

EDTA complex replacing heavy metals ions in solution. The result is named total hardness (providing the result for the total concentration of bivalent ions): total hardness (in mg equivalent $CaCO_3$/L) = $V_{EDTA} \cdot B / V_{sample}$, where B is mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant.

Water softening is conducted with ion-exchange resins strongly acidic (typically featuring sulfonic acid groups, RSO_3H, such as sodium polystyrene sulfonate). Softening has the purpose of replacing the Mg^{2+} and Ca^{2+} from water with Na^+: $2\text{-}SO_3Na + Ca^{2+} \rightarrow (\text{-}SO_3)_2Ca + 2Na^+$.

Procedure to be conducted by the technician when is necessary

Recharging the resin for water softening

Recharging of the resin for water softening should be conducted periodically since after each use of it, the Ca^{2+} and Mg^{2+} ions remain trapped into the resin and the resin become useless when no more retains these ions from solution. This moment is when a solution passed through the column still contains Ca^{2+} and Mg^{2+} ions (in greater proportions), and a titration with EDTA may reveal this. Then, the next steps should be followed:

÷ Washing it with a solution containing a high concentration of sodium ions (e.g. it has large amounts of common salt (NaCl) dissolved in it);

÷ The ions of calcium (Ca^{2+}) and magnesium (Mg^{2+}) migrate off the resin, being replaced by sodium ions from the solution until a new equilibrium is reached.

Standard Ca^{2+} solution

For standard Ca^{2+} solution, next steps should be followed:

÷ Weigh 1.000 g anhydrous $CaCO_3$ powder (primary standard or special reagent low in heavy metals, alkalis, and magnesium) into a 500 mL Erlenmeyer flask;

÷ Place a funnel in the flask neck and add, a little at a time, 1 + 1 HCl until all $CaCO_3$ has dissolved;

÷ Add 200 mL distilled water and boil for a few minutes to expel CO_2;

÷ Cool, add a few drops of methyl red indicator, and adjust to the intermediate (between red and yellow) orange colour by adding 3N NH_4OH or 1 + 1 HCl, as required;

÷ Transfer quantitatively and dilute to 1000 mL with distilled water.

Standard EDTA titrant preparation

For standard EDTA titrant of 0.01M concentration, next steps should be followed:

÷ Weigh 3.723 g EDTA (disodium ethylenediaminetetraacetate dihydrate, also called (ethylenedinitrilo)tetraacetic acid disodium salt) analytical reagent-grade;

÷ Dissolve it in distilled water, and dilute to 1000 mL;

÷ Standardize against standard Ca^{2+} solution;

÷ Then titrating with EDTA, 1mL EDTA corresponds to 1.00 mg $CaCO_3$ (the B constant above, to be written on the EDTA bottle).

Working procedure

Acidity and alkalinity of water

For *mineral acidity* follow the next steps (for two samples of about 100 ml of water from tap):

- In an Erlenmeyer flask (of about 300 ml) take a sample of water; record its volume (V_j);
- Add a drop of methyl orange indicator;
- Record the volume of NaOH from the burette ($V_{initial}$) in the table below;
- Titrate with NaOH the water sample till the moment in which a colour change is observed;
- Record the volume of NaOH from the burette (V_{final}) in the table below;

For *total acidity* repeat the steps from 'mineral acidity' replacing 'methyl orange indicator' with 'phenolphthalein indicator'.

For *total alkalinity* repeat the steps from 'mineral acidity' replacing 'NaOH' with 'HCl'.

For *permanent alkalinity* repeat the steps from 'mineral acidity' replacing 'NaOH' with 'HCl' and 'methyl orange indicator' with 'phenolphthalein indicator'.

Analysis	Water (ml)	Titrant	Indicator	$V_{initial}$	V_{final}	$(V_{final}-V_{initial})/V_i$	$\text{Average}((V_{final}-V_{initial})/V_i)$
mineral acidity	$V_1 =$	NaOH	methyl orange				$a_1 =$
	$V_2 =$						
total acidity	$V_3 =$	NaOH	phenolphthalein				$a_2 =$
	$V_4 =$						
total alkalinity	$V_5 =$	HCl	methyl orange				$a_3 =$
	$V_6 =$						
partial alkalinity	$V_7 =$	HCl	phenolphthalein				$a_4 =$
	$V_8 =$						

Table 4. Acidity and alkalinity of water samples

Hardness and softening of water

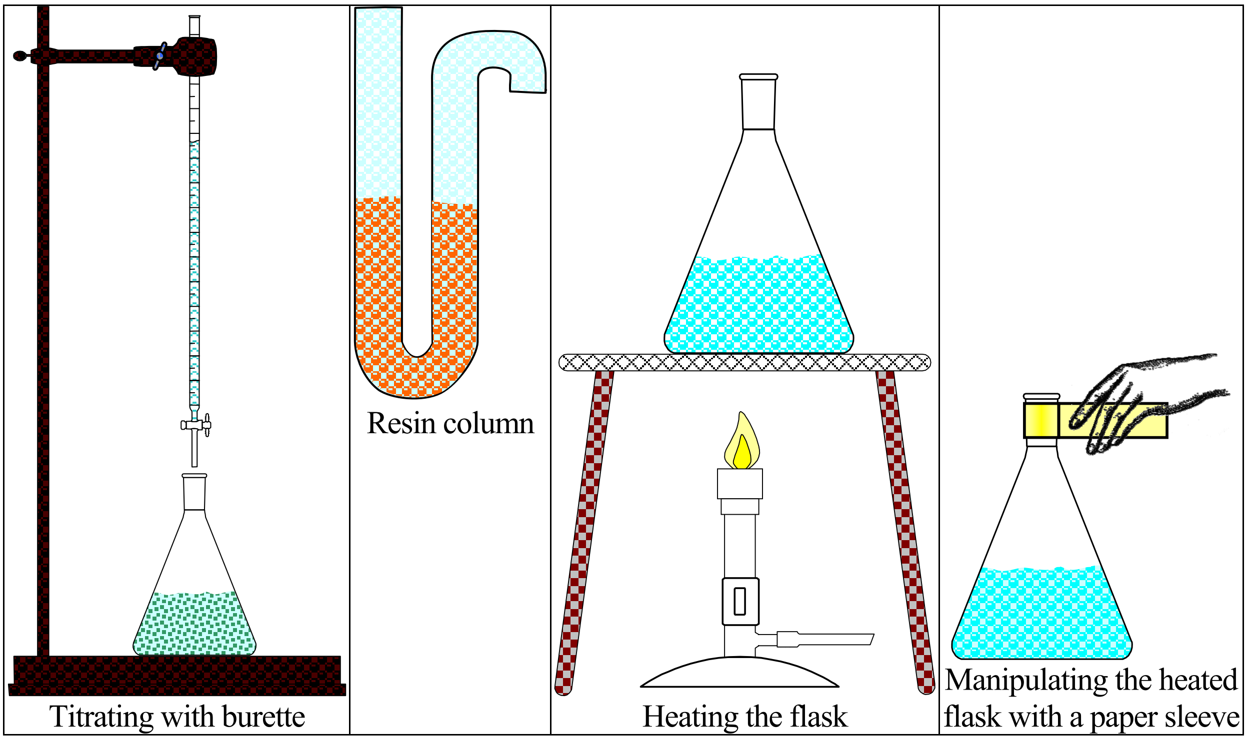
For *hardness* follow the next steps (for two samples of about 100 ml of water from tap):

- In an Erlenmeyer flask (of about 300 ml) take a sample of water; record its volume (V_j);
- Add HCl with 2 mL more than the average of (V_{final}-$V_{initial}$) needed for mineral acidity;
- Boil the sample in the flask for 5 minutes;
- Add 2 ml NaOH;
- Add 2 ml buffer (NH_4OH) solution (to provide a pH of 10±0.1);
- Add few crumbs of eriochrome black T indicator (till the solution become pale coloured);
- Record the volume of EDTA from the burette ($V_{initial}$) in the table below;
- Titrate with EDTA the water sample till the moment in which a colour change is observed;
- Record the volume of EDTA from the burette (V_{final}) in the table below;

For *softening* add water on the top of the resin column to collect two samples (see the figure) and then repeat the procedure measuring the hardness with the softened water, filling the values in the next table (Table 4).

Hardness	Water (ml)	Titrant	Indicator	$V_{initial}$	V_{final}	$(V_{final}-V_{initial})/V_i$	Average$((V_{final}-V_{initial})/V_i)$
regular	$V_1 =$	EDTA	eriochrome black T				$a_5 =$
	$V_2 =$						
softened	$V_3 =$						$a_6 =$
	$V_4 =$						

Table 4. Hardness of the regular and softened water



Titrating with burette

Resin column

Heating the flask

Manipulating the heated flask with a paper sleeve

Figure 1. Conducting the experiments

Data analysis

If a water contains only HO^-, HCO_3^- and CO_3^{2-} as significant bases, then the amount of H^+ required to reach the phenolphthalein endpoint is equal to the amount of HO^- plus the amount of CO_3^{2-} originally present ($H^+ + OH^- \rightleftharpoons H_2O$; $H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$, because at the pH = 8.3 where phenolphthalein changes its colour most of the alkalinity will be in the form of HCO_3^-. Any remaining HO^- or CO_3^{2-} would be exactly balanced by an equivalent amount of CO_2.

To reach the methyl orange endpoint, one must add an additional amount of H^+ to the amount of HCO_3^- present at the phenolphthalein endpoint: $H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O$. This will be equal to the amount of HCO_3^- plus CO_3^{2-} originally present since carbonate was entirely converted to bicarbonate in the first stage, and thus calculations of these species concentrations can be conducted (see Table 5).

Alkalinity	If $a_3/a_4 \leq 2$	If $a_3/a_4 \geq 2$
from HO^-	2·(partial alkalinity) - (total alkalinity)	0
from CO_3^{2-}	2·(total alkalinity - partial alkalinity)	2·(partial alkalinity)
from HCO_3^-	0	total alkalinity - partial alkalinity

Table 5. Approximate calculations from alkalinity of the water

Thus, stating from the experimental results (data from Table 4) calculations based on the formulas given (Table 2, Table 3 and Table 5) should be conducted, and the results are to be written in the water analysis bulletin below (Table 6).

Quantity	Value	Measurement unit
Used solutions		
÷ Concentration of NaOH solution	to be written	to be written
÷ Concentration of HCl solution	to be written	to be written
÷ Concentration of EDTA solution	to be written	to be written
Acidity and alkalinity		
÷ Mineral acidity	to be written	mg $CaCO_3$/L
÷ Total acidity	to be written	mg $CaCO_3$/L
÷ Difference (weak acids)	to be written	mg $CaCO_3$/L
÷ Partial alkalinity	to be written	mg $CaCO_3$/L
÷ Total alkalinity	to be written	mg $CaCO_3$/L
÷ Approximate alkalinity from HO^-	to be written	mg $CaCO_3$/L
÷ Approximate alkalinity from HCO_3^-	to be written	mg $CaCO_3$/L
÷ Approximate alkalinity from CO_3^{2-}	to be written	mg $CaCO_3$/L
Hardness of the water		
÷ Regular water	to be written	mg $CaCO_3$/L
÷ Softened water	to be written	mg $CaCO_3$/L

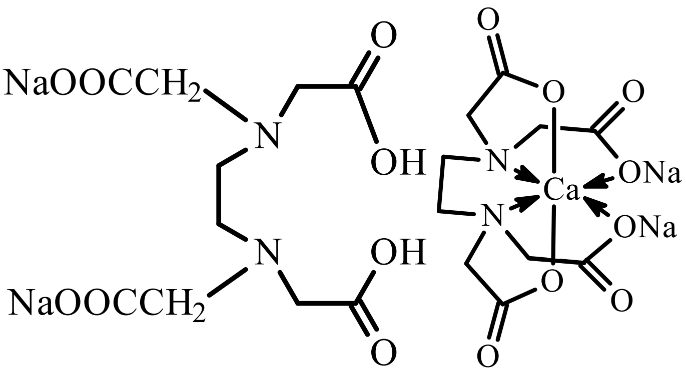
Table 6. Water analysis bulletin

Further reading

Complexometry

Complexometry (or chelatometry) is based on the formation of metal complexes with polycarboxylic acids and polyamines being improved method after 1940. During titration sample solution forms a stoechiometric complex soluble and undissociated. Techniques by which this operation is conducted are typical volumetric titration procedures. The general method has three main aspects: the choice of a suitable chelating agent, the choice of experimental conditions titration gives optimum (checking the pH and the presence of competitive ligands) and the choice of an appropriate method for the detection of the equivalence point. Complexation titrations combines the advantages and disadvantages of methods of titration in general and the formation of complexes: reaction product (complex) is undissociated, the complex does not give coprecipitation errors (like precipitation titrations), it have selectivity: complexing agent coordinates only certain metal ions, while the stoichiometry is not as well defined as in the titration of the precipitation, neutralization, or redox, if the complexing agent is an organic solvent, and therefore should pay attention to its solubility. Of these, the most used is ethylenediaminetetraacetic acid (EDTA), denoted symbolically H_4Y (namely the disodium salt of the acid, which is soluble in water denoted H_2YNa_2), with the structural formula in figure 2, along with logarithms of solubility constants for EDTA complexes of some metal ions. EDTA have 6 acidity constants, $pKa_{-2} = 0.0$, $pKa_{-1} = 1.5$, $pKa_1 = 2.0$, $pKa_2 = 2.66$, $pKa_3 = 6.16$, and $pKa_4 = 10.24$. This combination is known also under the name of Complexone III. It has the ability to form stable complexes, called complexones, with a large number of metals (Ca, Mg, Zn, Cd, Pb, Cu, Ni, Fe, etc.). These complexes are closing cycles (in this case of 5 atoms), and the chelating complexes are known to be very stable, but not coloured. Complexone III is widely used in chemical analysis to determine the displacement of many metals, by complexometric titration.

Group 1		Group 2		Group 3	
Mg	8.69	Mn	13.58	Hg	21.8
Ca	10.7	Fe	14.33	Bi	23
Sr	8.63	Rare earths	15.3-19.8	Co	36
Ba	7.76	Co	16.21	Cr	23
		Ni	18.56	Fe	25.1
		Cu	18.79	Ga	20.27
		Zn	16.5	In	24.95
		Cd	16.59	Sc	23.1
		Al	16.13	Sn	22
		Pb	18.3	Ti	17.7
		TiO	17.3	Tl	23.2
		V	12.7	V	25.9
		VO	18.77		



H_2YNa_2 (di-sodium salt of EDTA)
and
$CaYNa_2$ (or M, a bivalent metal)

Figure 2. Solubilities of the EDTA complexes by analytical groups of cations (expressed in pKa units)

An alternative is conducting previously a qualitative analysis, which may have the purpose of the increasing of the sensitivity (see for instance [217] and [218]). Other preliminary studies may include the molecular design (see [219], [220], [221], [222], [223], [224], [225], [226], [227] and [228]).

In order to indicate the equivalence point in complexometric titration, complexometric indicators are used. They are organic materials which form coloured complexes with metal ions, less stable than those of the respective metal complexone III. During titration with EDTA solution, which remove metal ions complex with the indicator, are formed the complexone which is more stable. At the end of the titration, at the equivalence point, the total amount of metal present in the sample is bound in the form of complexone (colourless), and the colour of the indicator solution appears clear. Most are using eriochrome black T complexometric indicators and murexide. Because EDTA is an acid, the pH depends on the stability of its complexes. Thus, in strongly acidic solution, the complex tends to release the metallic ion and reforming acid EDTA. Therefore complexometric titration is carried out in basic medium (in the presence of a basic buffer solution).

Species responsible for alkalinity and acidity in waters

Alkalinity and acidity can be interpreted in terms of concentrations of specific constituents only when the chemical composition of the water is known (this being the 'ideal' case). The species that provide alkalinity to water are bases and the species that provide acidity to water are acids. In unpolluted fresh waters, hydroxide, carbonate and bicarbonate are the most important bases. Therefore, total alkalinity is often approximated as the sum of the number of equivalents of these bases (minus the hydrogen ion concentration):

$$\text{Total alkalinity} \sim [HCO_3^-] + 2\cdot[CO_3^{2-}] + [HO^-] - [H^+]$$

In rare cases other bases may also be important such as the silicates, ammonia, phosphates, borates and organic bases. For example, extremely soft waters (total alkalinity < 10 mg $CaCO_3$/L) contain so little bicarbonate that ammonia and silicate concentrations become important. Aside from H^+ and OH^-, the anions found in fresh waters in order of importance are the carbonates, sulphate, chloride, silicate, organic anions, nitrate, fluoride, boron, bromide, ammonia and phosphate. Of these, sulphate, chloride, nitrate, fluoride and bromide are insufficiently basic to contribute to alkalinity regardless of their concentration. Similarly, most of the major cations such as calcium, sodium, magnesium, potassium and strontium do not hydrolyze to a sufficient extent within the pH range of interest to account for much alkalinity, and the remaining species of interest are listed in the next table (Table 7), along with their common molar concentration (c, in moles/L).

Species	c	Ref	pKa	Equilibrium
Carbonates	$1\cdot10^{-3}$	[229]	10.3	$CO_3^{2-} + 2H^+ \rightleftharpoons HCO_3^- + H^+$
			6.4	$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$
Silicates	$2\cdot10^{-4}$	[230]	9.8	$H_3SiO_4 + H^+ \rightleftharpoons H_4SiO_4$
Organics	$1\cdot10^{-4}$	[231]	3-10	$R\text{-}COO^- + H^+ \rightleftharpoons R\text{-}COOH$
Borates	$1\cdot10^{-6}$	[232]	9.2	$B(OH)_4^- + H^+ \rightleftharpoons B(OH)_3 + H_2O$
Ammonia	$2\cdot10^{-6}$	[233]	9.2	$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$
Iron	$2\cdot10^{-6}$	[234]	6.0	$Fe(OH)_4^- + 2H^+ \rightleftharpoons Fe(OH)_2^+ + 2H_2O$
			4.6	$Fe(OH)_2^+ + H^+ \rightleftharpoons Fe(OH)^{2+} + H_2O$
Aluminium	$2\cdot10^{-6}$	[235]	8.0	$Al(OH)_4^- + H^+ \rightleftharpoons Al(OH)_3 + H_2O$
			5.7	$Al(OH)_3 + H^+ \rightleftharpoons Al(OH)_2^+ + H_2O$
			4.3	$Al(OH)_2^+ + H^+ \rightleftharpoons Al(OH)^{2+} + H_2O$
			5.0	$Al(OH)^{2+} + H^+ \rightleftharpoons Al^{3+} + H_2O$
Phosphates	$7\cdot10^{-7}$	[236]	12.3	$PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}$
			7.2	$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$
			2.1	$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4$
Hydroxide	$2\cdot10^{-7}$	[237]	14.0	$OH^- + H^+ = H_2O$
Copper	$1\cdot10^{-7}$	[238]	9.8	$Cu(OH)_3^- + 2H^+ \rightleftharpoons Cu(OH)^+ + 2H_2O$
			7.3	$Cu(OH)^+ + H^+ \rightleftharpoons Cu^{2+} + H_2O$
Nickel	$2\cdot10^{-8}$	[239]	6.9	$Ni(OH)_2 + H^+ \rightleftharpoons Ni(OH)^+$
Cadmium	$1\cdot10^{-8}$	[240]	7.6	$Cd(OH)^+ + H^+ \rightleftharpoons Cd^{+2} + H_2O$
Lead	$1\cdot10^{-8}$	[241]	6.2	$Pb(OH)^+ + H^+ \rightleftharpoons Pb^{+2} + H_2O$
Sulphides	$2\cdot10^{-5}$	[242]	19.0	$S^{2-} + H^+ \rightleftharpoons HS^-$
			7.0	$HS^- + H^+ \rightleftharpoons H_2S$
Zinc	$8\cdot10^{-7}$	[243]	6.1	$Zn(OH)_2 + H^+ \rightleftharpoons Zn(OH)^+ + H_2O$
			9.0	$Zn(OH)^+ + H^+ \rightleftharpoons Zn^{2+} + H_2O$

Table 7. Species which contribute to the alkalinity of drinking waters

Based on the average concentrations shown here, the practice of interpreting fresh water alkalinity in terms of the carbonate system is justified. It is important to point out here that although carbonates contribute to alkalinity, the addition of carbon dioxide to water will not alter its alkalinity, because carbon dioxide consumes one hydroxide molecule for each bicarbonate molecule formed.

$$CO_2(aq) + OH^- \rightarrow HCO_3^-$$

The addition or loss of carbon dioxide might, however, result in a change in pH.

In contrast to fresh waters, seawater has such high concentrations of other bases, when the total alkalinity is usually expressed as:

$$\text{Total alkalinity} = [HCO_3^-] + 2\cdot[CO_3^{2-}] + [B(OH)_4] + [HPO_4^{2-}] + [H_3SiO_4] + [Mg(OH)^-] + [OH^-] - [H^+]$$

In industry, special processes may be involved for removing of specific compounds from aqueous and gaseous phase (see [56] and [57]) while environmental monitoring requires complex analysis involving the identification of the mechanisms (see [244]).

Volumetric and gravimetric methods in study of corrosion

Introduction

Corrosion is a gradual destruction of materials by chemical reaction with substances from their environment. Corrosion can occur in materials other than metals (such as ceramics or polymers), but in this context, the term degradation is more common.

Therefore, in the most common sense used, corrosion means electrochemical oxidation of metals in reaction with an oxidant (such as oxygen), typically producing oxide(s) or salt(s) of the metal. Rusting (the formation of iron oxides) is a well-known example of corrosion.

Many alloys corrode merely from exposure to moisture in air, and the process can be strongly affected by the presence of certain substances. Corrosion can occur locally to form a pit or crack, or it can extend across a wide (more or less uniformly) area at the surface (occurs on exposed surfaces being a diffusion-controlled process).

There are several methods to reduce the chemical activity at the exposed surface, such as passivation and electroplating.

Passivation involves a shielding outer-layer of base material, which can be applied as a microcoating, or which occurs spontaneously in nature. As a technique, passivation is the use of a light coat of a protective material, such as metal oxide, to create a shell against corrosion.

Electroplating is a process that uses electric current to reduce dissolved metal cations so that they form a coherent metal or alloy coating on a metal surface acting as an electrode. Electroplating is widely used in various industries for coating metal or alloy objects with a thin layer of a different metal or alloy or with a different composition of the same alloy. Anyway, the purpose is the same, to increase a material's corrosion resistance. Chromating is used for aluminium, zinc, cadmium, copper, silver, magnesium, and tin alloys while nickeling (nickel deposition) and galvanization (zinc deposition) is mainly used for iron alloys. Other alternatives are to do electroplate with an alloy (see [[245]]).

Gravimetric analysis is defined as the quantitative determination of quantities based on weight difference and eventually based on correspondences from chemical reactions. Mass is the most fundamental of all analytical measurements, and gravimetry is the oldest quantitative technique. Similarly, volumetric analysis is defines as the quantitative determination of quantities based on volume difference eventually based on correspondences from chemical reactions.

In both gravimetry and volumetry measurements can be conducted in all aggregation states (solid, liquid, gaseous) but in general are preferred solid state for gravimetry and liquid or gaseous state for volumetry. Both methods are chemical methods, meaning that the analysis is based on a change in the substance due to a chemical reaction and the measurements are conducted in absolute units (of mass and of volume).

Purpose

Two experiments of corrosion will be conducted, one in acidic environment for study of zinc corrosion and another one in basic environment for study of aluminium corrosion.

Material and method

In acidic aqueous (water based) environment zinc corrosion evolves by following reaction:

$$2H^{+}_{(aq)} + 1Zn_{(s)} \rightarrow 1H_{2(g)} + 1Zn^{2+}_{(aq)}$$

The previous given reaction is a 'total' one while hydrogen (H_2) leaves the reaction environment (aqueous solution) being released as gas (in the atmosphere). The corrosion in deep of the zinc sample may be prevented by deposition of a precipitate on the surface of the zinc (such as is ZnS when H_2S is used to provide the acidity). Useful information is about the solubility of the Zn salts in water, and therefore the next table provide the solubilities, expressed in mass fractions (see Table 1).

Salt	Solubility ($w_i = m_i/m$), as a function of temperature (in °C), when available
$ZnBr_2$	$w_i = 0.832_{\pm0.003} + 2.68_{\pm0.82} \cdot 10^{-4} \cdot \lvert t - 13.6_{\pm2.6} \rvert^{1.41_{\pm0.08}} - 5.795_{\pm1.295} \cdot 10^{-4} \cdot \lvert t - 35.6_{\pm1.3} \rvert^{1.25_{\pm0.08}}$
$Zn(CH_3COO)_2$	$w_i(t=20°C) = 0.231$
$ZnCO_3$	$w_i(t=20°C) = 4.692 \cdot 10^{-7}$
$ZnCl_2$	$w_i = 0.810_{\pm0.003} + 2.46_{\pm0.32} \cdot 10^{-3} \cdot (t-28.1_{\pm2.5})$ for $t < 28.1_{\pm2.5}$, $w_i = 0.810_{\pm0.003} + 6.66_{\pm0.54} \cdot 10^{-4} \cdot (t-28.1_{\pm2.5})$ otherwise
$Zn(ClO_3)_2$	$w_i = 0.6_{\pm N/A} + 0.1_{\pm N/A} / (1 + e^{-(t-15_{\pm N/A})/2.6_{\pm N/A}})$
$Zn(ClO_4)_2$	$w_i = 0.44_{\pm0.02} + 9_{\pm7} \cdot 10^{-4} \cdot t$
ZnI_2	$w_i = 0.858_{\pm0.009} - 0.046_{\pm0.007} \cdot e^{-0.5 \cdot (t/80_{\pm10})^2}$
$Zn(IO_3)_2$	$w_i = 2.7_{\pm0.2} \cdot 10^{-3} + 1.85_{\pm0.11} \cdot 10^{-4} \cdot t - 1.5_{\pm0.2} \cdot 10^{-6} \cdot t^2$
$Zn(NO_3)_2$	$w_i = 0.49_{\pm0.06} + 0.39_{\pm0.10} / (1 + e^{-(t-35_{\pm5})/6.4_{\pm4.6}})$
$ZnSO_3$	$w_i = 1.768_{\pm0.002} \cdot 10^{-3} + 8.7_{\pm0.4} \cdot 10^{-7} \cdot t$
$ZnSO_4$	$w_i = 0.434_{\pm0.003} + 3.06_{\pm0.06} \cdot 10^{-3} \cdot (t-47.2_{\pm0.6})$ for $t < 47.2_{\pm0.6}$, $w_i = 0.434_{\pm0.003} - 1.09_{\pm0.05} \cdot 10^{-3} \cdot (t-47.2_{\pm0.6})$ otherwise

Table 1. Solubilities of some Zn salts in water

As can be seen from the previous table (see Table 1) high solubilities favouring the continuation of the corrosion process in the deep of the metal are for the salts of Zn with Iodine (ZnI_2), Bromine ($ZnBr_2$), Chlorine ($ZnCl_2$), as well as for $ZnSO_4$, $Zn(NO_3)_2$, $Zn(ClO_3)_2$, and $Zn(ClO_4)_2$ in this descending order. Thus, is expected that Zn to be efficiently corroded in aqueous environments of HI, HBr, HCl, H_2SO_4, HNO_3, $HClO_3$, and $HClO_4$.

In basic aqueous (water based) environment aluminium corrosion evolves by following reaction:

$$6H_2O_{(l)} + 2HO^{-}_{(aq)} + 2Al_{(s)} \rightarrow 3H_{2(g)} + 2Al(OH)_4{}^{-}_{(aq)}$$

The previous given reaction is a 'total' one while hydrogen (H_2) leaves the reaction environment (aqueous solution) being released as gas (in the atmosphere). The corrosion in deep of the aluminium sample may be prevented by deposition of a precipitate on the surface of the aluminium.

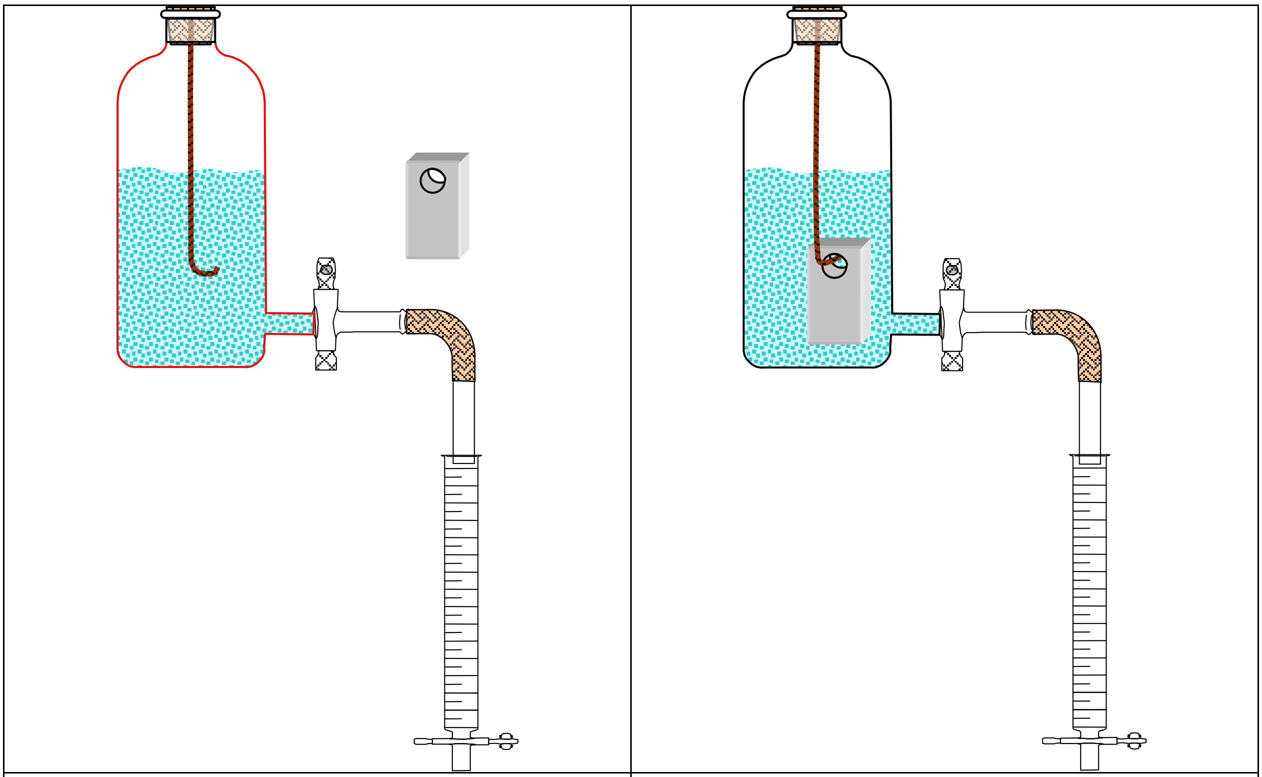
In presence of other metallic ions, such as Na^+ and K^+, in the first stage is formed a double oxide ($NaAlO_2$ or $KAlO_2$), which later absorbs different quantities of water in its solid structure (see [246]) depending on the temperature:

$$2Al + 2NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow 2NaAlO_{2(s)} + 3H_{2(g)}$$

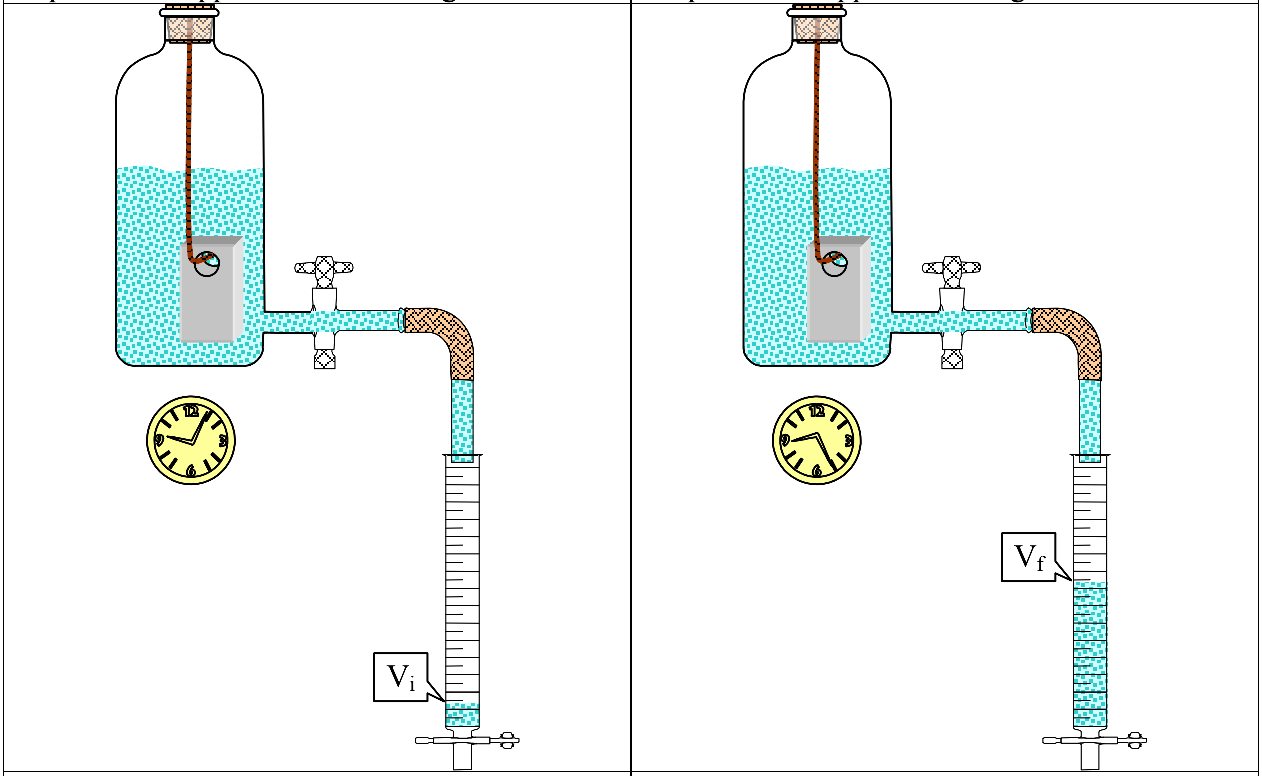
$$2NaAlO_2 + 3H_2O \rightarrow 2NaAlO_2\cdot{}^{3}/_{2}H_2O \text{ at 5-45°C}$$

$$4NaAlO_2 + 5H_2O \rightarrow 4NaAlO_2\cdot{}^{5}/_{4}H_2O \text{ at 60-140°C}$$

The experimental apparatus for zinc corrosion is assembled and the experiment is conducted as is illustrated below (see Figure 1).



Experimental apparatus before using for corrosion | Experimental apparatus during use for corrosion



Starting the chronometer for corrosion of Zn | Stopping the chronometer for corrosion of Zn

Figure 1. Study of the corrosion of zinc by volumetric method

The experimental apparatus for aluminium corrosion is assembled and the experiment is conducted as is illustrated below (see Figure 2).

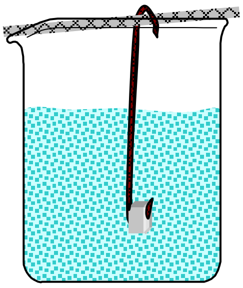


Figure 2. Study of the corrosion of aluminium by gravimetric method

Working procedure

Corrosion of zinc

The succession of the steps is as follows (data to be filled in Table 2):

- Take the sample, polish (with abrasive paper) and degreases it (with limewater, $Ca(OH)_2$) if is necessary;
- Measure the surface of the sample (by using the ruler) and record the value (S);
- Open the corrosion vessel, fix the sample in its support and put the cork assuring that no air is allowed to pass in the vessel;
- Open the valve to allow the liquid to pass out from the vessel and to pass in the burette;
- Wait a little time till the liquid flows with constant speed;
- In the same moment, record the level of the liquid in the burette ($V_i = V_1$) and start the timer (t_1);
- After a while, in the same moment record the level of the liquid in the burette ($V_f = V_2$) and stop the timer (t_2);
- Close the valve which allow the liquid to pass out from the vessel;
- Remove the sample from the vessel by taking the cork with which the sample is connected.

S	$V_i = V_1$	$V_f = V_2$	ΔV	$\Delta t = t_2 - t_1$
cm^2	ml	ml	ml	s

Table 2. Experimental data from corrosion of zinc

Corrosion of aluminium

The succession of the steps is as follows (data to be filled in Table 3):

- Take the sample, polish (with abrasive paper) and degreases it (with limewater, $Ca(OH)_2$) if is necessary;
- Measure the surface of the sample (by using the ruler) and record the value (S);
- Weight the sample using the analytical balance and record the value (m_1);
- Fix the sample in its support, place it into the corrosion vessel and start the timer (t_1);

- After a while (about 15 minutes) stop the timer (t_2) and remove the sample from the corrosion vessel;
- Use a paper filter or something else rough to clean the surfaces of the sample;
- Weight the sample again (m_2).

S	m_1	m_2	$\Delta m = m_2 - m_1$	$\Delta t = t_2 - t_1$
cm^2	g	g	g	s

Table 3. Experimental data from corrosion of aluminium

- In order to conduct the required calculations about the corrosion, are necessary to take the values of the temperature and of the pressure from the laboratory, using the barometer and thermometer available in the laboratory. Let's label these values with T (for temperature, in K) and p (for pressure, in cmHg). The values are to be written in Table 4, where are given also the standard values for the temperature (T_0) and the pressure (p_0) as well as the densities and the molar masses of the metals.

T	p	T_0	p_0	ρ_{Zn}	ρ_{Al}	M_{Zn}	M_{Al}
K	cmHg	K	cmHg	kg/m^3	kg/m^3	g/mole	g/mole
		273.15	75.6	2700	7140	65.38	26.982

Table 4. Experimental conditions during corrosion

Data analysis

The subject of the data analysis is to assess the class of corrosion as well as to calculate the volume of the hydrogen released during the process. Depending on the corrosion rate the materials can be classified as in the Table 5.

Class	C1	C2	C3	C4	C5	C6
Corrosion rate (μm/year)	< 0.1	[0.1, 0.32)	[0.32, 1.00)	[1.00, 3.20)	[3.20, 10.00)	≥ 10
Name	Very low	Low	Medium	High	Very high	Extremely

Table 5. Classes of corrosion

The released hydrogen is considered to be an ideal gas, and therefore its volume in standard conditions can be obtained from the volume of the hydrogen released in the conditions exiting in the laboratory by using the relationship of transformation to the standard conditions.

To calculate the volume of the hydrogen released during corrosion of the zinc is immediately from the volume of the liquid collected in the burette (which is equal in volume with the released hydrogen). In order to obtain the quantity of metal consumed in the reaction, it must be call for the equation of the chemical reaction. When 1 mole of hydrogen (H_2) is released, 1 mole of Zn is consumed, and the number of moles of zinc is equal with the number of moles of H_2 released. The number of moles of hydrogen can be calculated from its volume in standard conditions (1 mole of ideal gas occupies $V_0 = 22.711$ dm^3 at 0 °C and 10^5 Pa), and the number of moles of Zn is immediate. To obtain the mass of the zinc consumed is necessary to express its mass from the number of moles, and to obtain its volume is necessary to use the density.

To calculate the volume of the hydrogen released during corrosion of the aluminium is necessary to calculate first its number of moles from the quantity of metal consumed in the reaction, by calling for the equation of the chemical reaction. When 3 moles of hydrogen (H_2) are released, 2 moles of Al are consumed. The number of moles of hydrogen can be used to obtain its volume in standard conditions (1 mole of ideal gas occupies $V_0 = 22.711$ dm^3 at 0 °C and 10^5 Pa), the number of moles of Al being immediate from its mass. To obtain the volume of the aluminium consumed is necessary to express its volume by using the density.

The volume divided by the surface provides the penetration deep. In order to obtain the corrosion rate by year, this penetration deep should be divided by the corrosion time (in s) and multiplied with the number of seconds in 365 days (31536000 s).

Following table is to be filled (Table 6) for corrosion of Zn.

Parameter	Measure	Unit	Value	Calculation hint
Surface	S	cm^2		from Table 2
Corrosion time	Δt	s		from Table 2
Volume of H_2	$\Delta V(H_2)$	ml		from Table 2
Standard volume of H_2	$\Delta V_{STD}(H_2)$	dm^3		$\Delta V_{STD} = \Delta V \cdot (p/p_0) \cdot (T_0/T)$
Number of moles of H_2	$\Delta n(H_2)$	moles		$\Delta n = \Delta V \cdot (p/p_0) \cdot (T_0/T)/V_0$
Number of moles of Zn	Δn(Zn)	moles		$2H^+_{(aq)} + 1Zn_{(s)} \rightarrow 1H_{2(g)} + 1Zn^{2+}_{(aq)}$
Mass of Zn corroded	Δm(Zn)	g		$\Delta m = \Delta n \cdot M$
Volume of Zn corroded	ΔV(Zn)	m^3		$\Delta V = \Delta m/\rho$
Penetration deep in Zn	Δh(Zn)	m		$\Delta h = \Delta V/S$
Penetration rate	v(Zn)	μm/year		$v = \Delta h/\Delta t$
Resistance class	of Zn	C1-C6		from Table 5

Table 6. Calculations for the corrosion of Zn

Following table is to be filled (Table 7) for corrosion of Al.

Parameter	Measure	Unit	Value	Calculation hint
Surface	S	cm^2		from Table 2
Corrosion time	Δt	s		from Table 2
Mass of Al corroded	Δm(Al)	g		from Table 2
Number of moles of Al	Δn(Al)	moles		$\Delta n = \Delta m/M$
Number of moles of H_2	$\Delta n(H_2)$	moles		$2Al + 2NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow 2NaAlO_{2(s)} + 3H_{2(g)}$
Standard volume of H_2	$\Delta V_{STD}(H_2)$	dm^3		$\Delta V_{STD} = \Delta n \cdot V_0$
Volume of H_2	$\Delta V(H_2)$	ml		$\Delta V = \Delta V_{STD} \cdot (p_0/p) \cdot (T/T_0)$
Volume of Al corroded	ΔV(Al)	m^3		$\Delta V = \Delta m/\rho$
Penetration deep in Al	Δh(Al)	m		$\Delta h = \Delta V/S$
Penetration rate	v(Al)	μm/year		$v = \Delta h/\Delta t$
Resistance class	of Al	C1-C6		from Table 5

Table 7. Calculations for the corrosion of Al

Nickel corrosion protective electroplating

Introduction

Electroplating is a surface covering in which a metal is deposited on a conductive surface. It is used to decorate objects, for corrosion inhibition, to improve solderability, to harden, to improve wearability, to reduce friction, to improve paint adhesion, to alter conductivity, to improve IR reflectivity, for radiation shielding, and for other purposes.

In electroplating, an ionic metal is supplied with electrons to form a non-ionic coating on a substrate. A common system involves a chemical solution with the ionic form of the metal, an anode (positively charged) which may consist of the metal being plated (a soluble anode) or an insoluble anode (usually carbon, platinum, titanium, lead, or steel), and finally, a cathode (negatively charged) where electrons are supplied to produce a film of non-ionic metal.

Chrome plating is a finishing treatment using the electrolytic deposition of chromium. The most common form of chrome plating is the thin, decorative bright chrome, which is typically a 10-µm layer over an underlying nickel plate. When plating on iron or steel, an underlying plating of copper allows the nickel to adhere. The pores (tiny holes) in the nickel and chromium layers work to alleviate stress caused by thermal expansion mismatch but also hurt the corrosion resistance of the coating. Corrosion resistance relies on what is called the passivation layer, which is determined by the chemical composition and processing, and is damaged by cracks and pores. In a special case, micropores can help distribute the electrochemical potential that accelerates galvanic corrosion between the layers of nickel and chromium. Depending on the application, coatings of different thicknesses will require different balances of the aforementioned properties. Thin, bright chrome imparts a mirror-like finish to items such as metal furniture frames and automotive trim. Thicker deposits, up to 1000 µm, are called hard chrome and are used in industrial equipment to reduce friction and wear.

Nickel plating is usually conducted for steels, copper and copper alloys, and zinc and zinc alloys. When nickel is electrodeposited for corrosion protective plating, the thick of the nickel layer provide the class of the protective plate (see Table 1).

Grade	A	B	C	D	E	F	G
Thick (inches)	0.0016	0.0012	0.0010	0.0008	0.0006	0.0004	0.0002
Thick (µm)	40.6	30.5	25.4	20.3	15.2	10.2	5.1

Table 1. Grades for Nickel deposition

Purpose

Two experiments of nickel deposition will be conducted, one following the prescriptions for a good nickel deposition when the yield of the use of the electric current will be subject of calculation and the other one, by using a higher density of current with less electroplating time, when a qualitative analysis of the deposition will be conducted seeking for pores.

Material and method

Deposition of nickel by electroplating is usually conducted having nickel cations in the bath in which the nickel plating is conducted.

Then the metallic object is connected at the cathode of a power source and at the anode of the power source is connected a piece of nickel.

In the absence of the electric current nothing happens. In order to pass the nickel cations from the solution to the cathode (and to pass the nickel atoms from the metallic piece into the solution as cations) is necessary to assure a minimum difference of potential between the two electrodes. The standard electrode potential for the reduction of Ni^{2+} is -0.25V, and thus when more than this difference of potential is assured, following chemical reactions occurs (Table 2).

Electrode	Connected with	Half-reaction	Remarks
Cathode (-)	Metallic piece	$Ni^{2+} + 2e^- \rightarrow Ni^0$	Nickel is deposited on the metallic piece from solution
Anode (+)	Nickel piece	$Ni^0 - 2e^- \rightarrow Ni^{2+}$	Nickel is dissolved in the electrolysis solution

Table 2. Half-reactions for nickel deposition

High densities of current must be avoided, because at high densities of current oxygen anions (O^{2-}) have the tendency to discharge at the anode ($O^{2-} - 2e^- \rightarrow O^0$) when the atomic oxygen combines with the nickel from the surface of the nickel piece, creating a layer of nickel oxide (NiO) which prevent dissolving of the nickel in the electroplating solution. As consequence, the solution becomes highly acidic, with less and less nickel ions dissolved in.

Electroplating solutions for nickel deposition are sensitive to pH. The pH should be between 5.4 and 6 and in order to provide this pH, along with a nickel salt is dissolved too an acid (sulphuric, boric or citric).

Electrical conductivity of nickel salts solutions is relatively small. In order to improve the conductivity, conductibility salts are added. These salts should have cations which discharge at cathode at higher potentials (in order to prevent the deposition of these cations in place of nickel cations) but with higher dissociation degree to provide carriers for the electrical charge. Examples of such kind of salts includes $(NH_4)_2SO_4$, NH_4Cl, Na_2SO_4 and NaCl. Chlorides help the dissolving of the nickel from the anode, but in the same time the higher density of nickel cations in solution provides a too fast deposition of nickel on the cathode, creating small crystals of nickel at the surface of the metallic piece, with reduced resistance to corrosion, and therefore nickel sulphate salt is the preferred alternative. In order to provide many crystallisation seeds a salt of magnesium sulphate is added, providing thus a more uniform deposition of nickel. Thus a special care must be provided for the preparation of the electrolysis solution. The recipe to prepare the electrolysis solution is given in the next table (see Table 3; to be dissolved in 0.3 L of water and after dissolving to be completed with water at 0.5 L).

Substance	Quantity	Role
$NiSO_4 \cdot 7H_2O$	68g	Source of Ni^{2+}
NH_4Cl	8g	For conduction
$MgSO_4 \cdot 7H_2O$	24g	Crystallisation seedling
H_3BO_3	2g	Buffering the pH

Table 3. Recipe for preparing the electrolysis solution for nickel deposition

The quality of the nickel deposition depends on the density of current. At too small current densities the deposition is slow, the nickel crystals will grow higher and the layer deposited will be soft and mat. At too high current densities, the nickel will be deposited as dust, the bonds between atoms being irregularly created, and the layer have then a black colour. The optimal density of current depends on the composition and on the size of the nickel deposition bath. For the bath to be used in the laboratory experiment the optimal current density is $D_C = 0.5$ A/dm^2. The determination of the optimal current density involves a series of preliminary experiments with the Hull cell [247].

The experiment of nickel plating is conducted using an electrolytic bath connected to a power source (U) being interconnected using a variable resistor (R) and an ampere-meter (A).

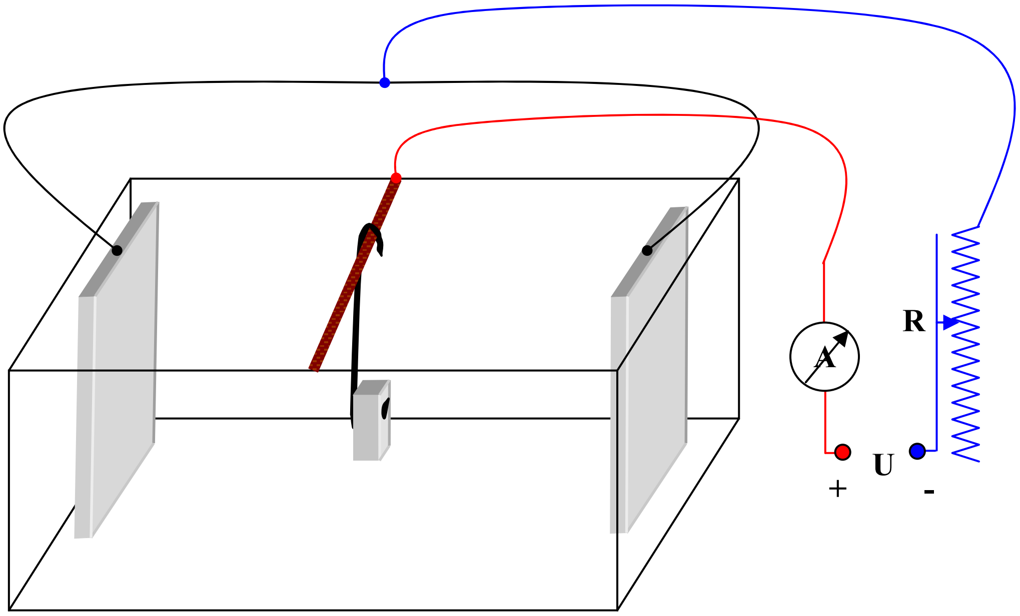


Figure 1. Instrumentation for nickel plating

Working procedure

Experiment for efficiency of nickel deposition

The succession of the steps is as follows (data to be filled in Table 4):

- Take the (biggest) sample, polish (with abrasive paper) and degreases it (with limewater, $Ca(OH)_2$) if is necessary;
- Measure the surface of the sample (by using the ruler) and record the value (S); piece have two sides, so please take it both into account;
- Calculate the ideal current intensity (I_{thr}) by using the ideal density of current ($D_C = 0.5$ A/dm^2);
- Weight the sample using the analytical balance and record the value (m_1);

- Place the sample in the bath;
- Connect the power source and start the timer (t_1);
- Adjust the intensity of the current using the potentiometer (R) to the nearest (to the ideal value) division on the ampere-meter and record the value (I_{exp});
- After a while (about 15 minutes), in the same moment unplug the power source and stop the timer, recording its value (t_2);
- Weight the sample again using the analytical balance and record the value (m_2).

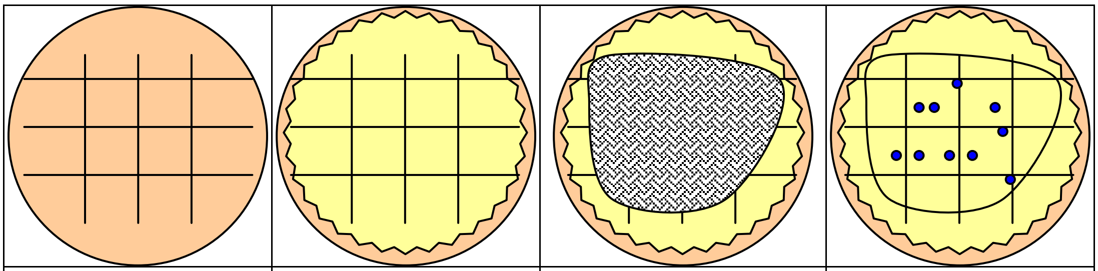
S	I_{thr}	I_{exp}	m_1	m_2	t_1	t_2
cm^2	A	A	g	g	hh:mm:ss	hh:mm:ss

Table 4. Experimental data from nickel plating

Experiment for quality of nickel deposition

The succession of the steps is as follows:

- Take the (smallest) sample, polish (with abrasive paper) and degreases it (with limewater, $Ca(OH)_2$) if is necessary;
- Place the sample in the bath;
- Connect the power source; please do not adjust the intensity of the current;
- After a while (about 5 minutes), unplug the power source;
- Clean the sample with water;
- Divide with a pencil filter paper into parts of $1cm^2$ (see Figure 2);



Marked filter paper | Soaked filter paper | With sample in contact | Iron pores reacted

Figure 2. Qualitative study of nickel deposition

- Soak the filter paper with $K_3Fe(CN)_6$;
- Place the sample onto the filter paper (for one minute); iron from the surface of the sample if exists reacts with $K_3Fe(CN)_6$ providing an intense blue coloured spot, from the reaction: $3Fe^{2+} + 2K_3Fe(CN)_6 \rightarrow 1Fe_3[Fe(CN)_6]_2 + 6K^+$;
- Take the sample out from the filter paper and count the number of pores in each square, filling the result in the next table (Table 5);

Surface	S11	S12	S21	S22	Average
Pores					

Table 5. Experimental data from qualitative study of nickel deposition

Data analysis for efficiency of nickel deposition

In order to assess the efficiency of nickel deposition the theoretical mass of nickel must be calculated by using the electrolysis law:

$$\Delta m_{thr} = \frac{M(Ni) \cdot I_{exp} \cdot \Delta t_{exp}}{n_{e^-}(Ni) \cdot F}; \ \eta = 100 \cdot \frac{\Delta m_{exp}}{\Delta m_{thr}} \ [\%]$$

where:

÷ M(Ni) is the molar mass of Ni, M(Ni) = 58.693 g/mol;

÷ I_{exp} is the intensity of the current used in the experiment of nickel plating (from Table 4);

÷ Δt_{exp} is the time while nickel were deposited on the sample;

÷ n_{e-} is the number of electrons exchanged at the deposition ($Ni^{2+} + 2e^- \rightarrow Ni^0$);

÷ F is the Faraday's constant, F = 96500 A·s;

S	I_{exp}	$\Delta m_{exp} = m_2 - m_1$	$\Delta t_{exp} = t_2 - t_1$	Δm_{thr}	η	Δh	Grade
cm^2	A	g	s	g	%	µm	A-G

Table 6. Data analysis from nickel plating

In order to evaluate the average thickness of the deposited nickel, the practical mass of the deposited nickel is converted into units of volume by using the density of nickel ($\Delta V_{exp} = \Delta m_{exp}/\rho$, $\rho(Ni) = 8908$ $kg \cdot m^{-3}$) and the thick (Δh) is obtained dividing this volume to the surface ($\Delta h = \Delta V_{exp}/S$).

Producing electricity from electrochemical cells

Introduction

An electrochemical cell is a device capable of either generating electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy.

An electrochemical cell can be created by placing electrodes into an electrolyte where a chemical reaction either uses or generates an electric current (see Table 1). Electrochemical cells which generate an electric current are called voltaic cells or galvanic cells while in the other electrochemical cells an externally supplied electric current is used to drive a chemical reaction which would not occur spontaneously, and such cells are called electrolytic cells.

Redox (reduction and oxidation) reactions take place in electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells and then the electric current may be produced from it, while nonspontaneous reactions occur in electrolytic cells and then the electric current is necessary to it. Both types of cells contain two electrodes (anode and cathode) where the oxidation and reduction reactions occur. Naming convention is that the oxidation occurs at the electrode named anode and reduction occurs at the electrode named cathode. Thus, in both galvanic and electrolytic cells, oxidation takes place at the anode, reduction takes place at the cathode, and electrons flow from the anode to the cathode (see Table 1).

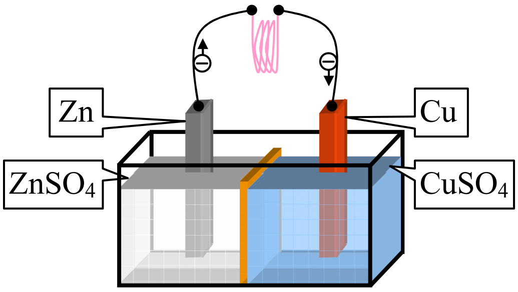
Cell	Reaction	Anode	Cathode	Electrical current
Galvanic	Spontaneous	Negative	Positive	Is produced during the chemical reaction
Electrolytic	Nonspontaneous	Positive	Negative	Is consumed to produce the chemical reaction

Table 1. Naming conventions for electrochemical cells

Common batteries consist of one or more galvanic cells. A galvanic cell can be created using as electrodes any two different metals since metals differ in their tendency to lose electrons. Zinc more readily loses electrons than copper, so placing zinc and copper metal in solutions of their salts can cause electrons to flow through an external wire which leads from the zinc to the copper. As a zinc atom provides the electrons, it becomes a positive ion and goes into aqueous solution, decreasing the mass of the zinc electrode. On the copper side, the two electrons received allow it to convert a copper ion from solution into an uncharged copper atom which deposits on the copper electrode, increasing its mass.

Half-reaction	Type	Electrode	Charge	Potential
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$	oxidation	anode	negative	+0.763
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	reduction	cathode	positive	+0.337

Table 2. Typical example of a galvanic cell (Daniell)



The two reactions are typically written (letters in parentheses are reminders that the zinc goes from a solid (s) into an aqueous solution (aq) and vice versa for the copper). It is typical in the language of electrochemistry to refer to these two processes as "half-reactions" which occur at the two electrodes.

Purpose

Three experiments of measurement of the electromotive force (potential) will be conducted: for the Daniell cell, for a typical battery, and for a photovoltaic cell.

Material and method

The experiment designed for measurements with the Daniell's galvanic cell is depicted in the Figure 1, the battery in Figure 2 and the photovoltaic cell in Figure 3.

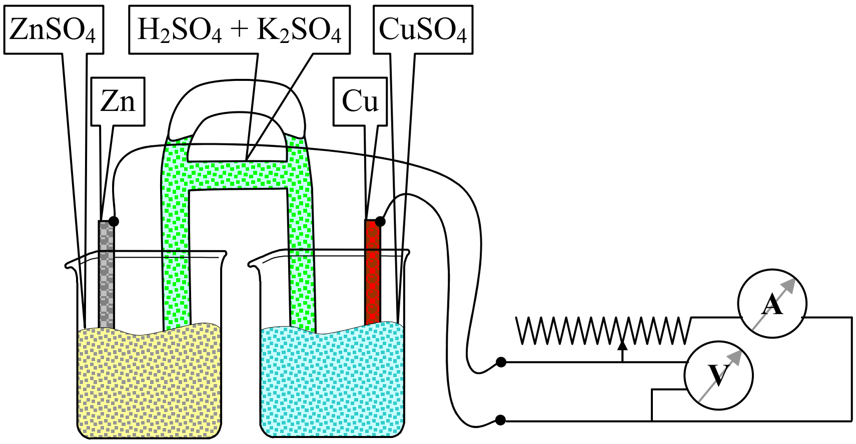


Figure 1. Measurements with Daniell's galvanic cell

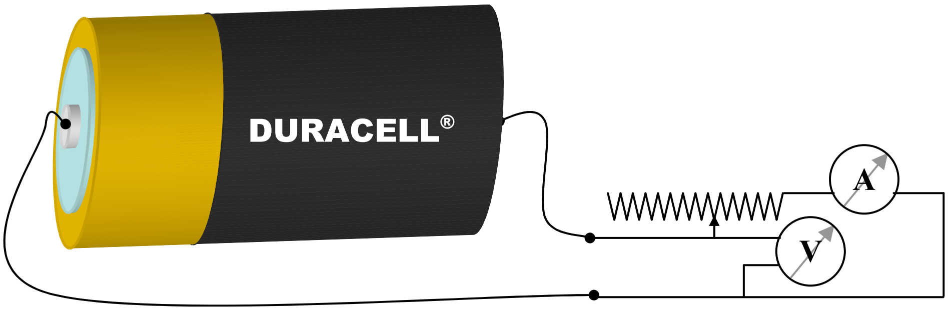


Figure 2. Measurements with Duracell battery

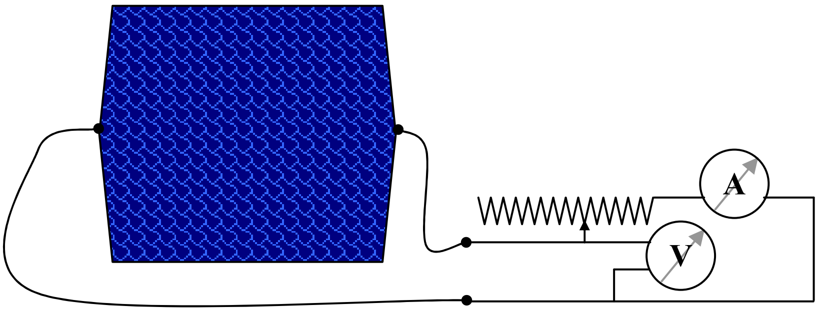


Figure 3. Measurements with photovoltaic cell

The galvanic cell (Figure 1) consists from two cups, one containing a solution of $ZnSO_4$ in which is immersed a Zn electrode, the other containing a solution of $CuSO_4$ in which is immersed a Cu electrode. The ions transfer from one cup to another is possible through a bridge containing a solution with same anion (SO_4^{2-}) as the solutions from the cups. At each electrode a chemical equilibrium is established. Being more chemically active, zinc have the tendency to pass in the solution, and copper being less active, have the tendency to precipitate on the electrode. The overall chemical process is possible when electrons are allowed to move through the external circuit.

Cylindrical alkaline batteries are produced with a high surface area zinc anode, a high density manganese dioxide cathode, and a potassium hydroxide electrolyte. Battery produces electricity when the manganese dioxide cathode is reduced and the zinc anode becomes oxidized. The global equation is as follows:

$$1Zn + 2MnO_2 + 1H_2O \rightarrow 1ZnO + 2MnOOH$$

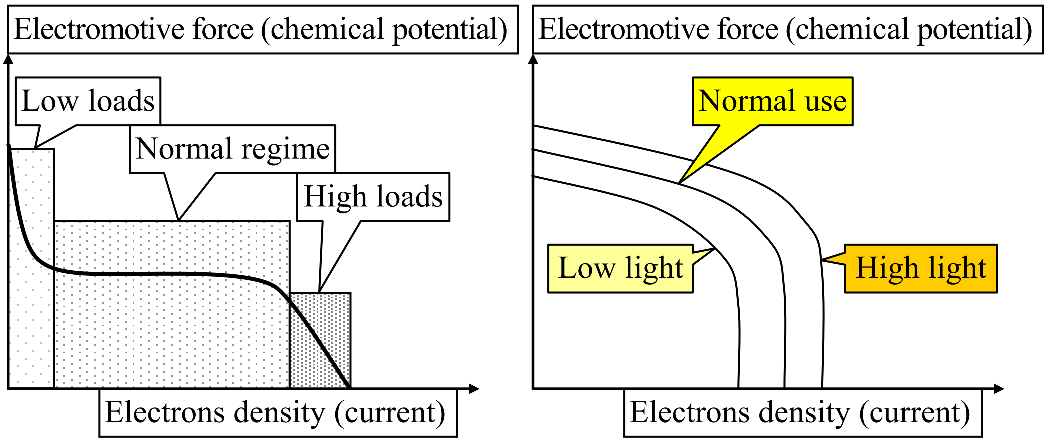
During this reaction, water (H_2O) is consumed and hydroxyl ion (OH^-) are produced by MnO_2 cathode under following reaction:

$$2MnO_2 + 2H_2O + 2e^- \rightarrow 2MnOOH + 2OH^-$$

At the same time, the anode is consuming hydroxyl ions and is producing water:

$$1Zn + 2OH^- \rightarrow 1ZnO + 1H_2O + 2e^-$$

Typical solar cells are made from amorphous silicon deposited in thin films in an atmosphere of Ar and H_2 when p-n junctions are created and photovoltaic effect is exhibited. The photovoltaic cell needs to have some spatial asymmetry such as is the contact surface between two semiconductors with different electronic properties in order to drive the excited by light electrons through the external circuit. The extra energy of the excited electrons generates a potential difference (the electromotive force).



Typical battery Typical solar cell

Figure 4. Working regime of two chemical sources of electrical energy

There are some differences between conventional chemical sources of energy - the batteries - and unconventional ones - photovoltaic cells, as are depicted in Figure 4. It is expected that the solar cell to provide a constant current for any illumination level while the voltage to be determined by the resistance of the load. The main difference consists in the internal resistance: the photovoltaic cell have much higher (than the battery) internal resistance, and thus is expected that the photovoltaic cell to act as a current source, while the battery to act as a voltage source.

Working procedure

For each experiment (out of three) the succession of the steps is as follows (data to be filled in Table 3):

- Connect the external load (variable resistance, ampere-meter and voltmeter) to the cell;
- Adjust the load (using the variable resistance) to have on both apparatus the values inside of the scale of measurement;
- Take one measurement of the voltage (U) and of the intensity (I);
- Adjust the load (using the variable resistance) while both apparatus indicate a sensitive change of the measured values;
- Take the second measurement of the voltage (U) and of the intensity (I);
- Continue (in same direction) to adjust the load (using the variable resistance) while both apparatus indicate a sensitive change of the measured values;
- Take the third measurement of the voltage (U) and of the intensity (I);
- For the photovoltaic cell is preferable to take two more measurements.

Daniell's cell			Battery			Solar cell		
No	Voltage (U)	Intensity (I)	No	Voltage (U)	Intensity (I)	No	Voltage (U)	Intensity (I)
1	$V_1 =$	$I_1 =$	1	$V_1 =$	$I_1 =$	1	$V_1 =$	$I_1 =$
2	$V_2 =$	$I_2 =$	2	$V_2 =$	$I_2 =$	2	$V_2 =$	$I_2 =$
3	$V_3 =$	$I_3 =$	3	$V_3 =$	$I_3 =$	3	$V_3 =$	$I_3 =$
						4	$V_4 =$	$I_4 =$
						5	$V_3 =$	$I_5 =$

Table 3. Experimental data from chemical cells measurements

Data analysis for electromotive force of the chemical cells

It's expected to obtain a linear dependence of the voltage relative to intensity for the Daniell's cell and the battery and it's expected to be a nonlinear dependence for the solar cell.

Let's consider the electrical circuit associated with the experiment (see Figure 5).

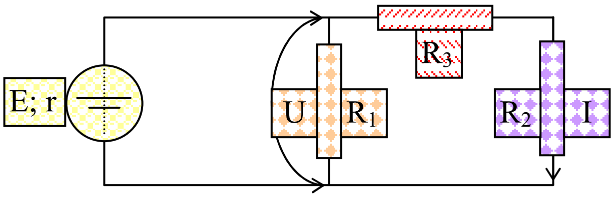


Figure 5. Electrical circuit used in the measurements

Applying the continuous current laws for the circuits (Kirchhoff's laws) and for the consumers

(Ohm's law) following equations can be obtained:

- $E = I_0 \cdot r + U$ for the circuit containing the source and the voltmeter ($U = I_1 \cdot R_1$);
- $E = I_0 \cdot r + I \cdot R_3 + I \cdot R_2$ for the circuit containing the source and the ampere-meter ($I_0 = I + I_1$);

The subjects of findings are E and r, and the known values are U and I. Thus, substituting: $E - U = (I + I_1) \cdot r$, $E = (I + I_1) \cdot r + I \cdot (R_3 + R_2) = E - U + I \cdot (R_3 + R_2) \rightarrow U = I \cdot (R_3 + R_2)$ and the two equations are reduced to only one: $E - U = (I + I_1) \cdot r$ which contain also the intensity of current passing trough the voltmeter (I_1).

Usually it's expected that $I_1 << I$ because most of the voltmeters are designed such that to have a very high internal resistance ($R_1 >> r$, $R_1 >> R_2$, $R_1 >> R_3$) and thus I_1 intensity may become negligible relative to the others ($I_1 << I$, $I_1 << I_0$). By using this approximation, the equation becomes: $E - U = I \cdot r$ which still contains two unknowns (E and r).

How is possible to solve a mathematical equation with two unknowns? The magic may come from experiments: collecting different values for U and I while E and r remains the same and this is what we done (see Table 3): $E - V_1 = I_1 \cdot r$; $E - V_2 = I_2 \cdot r$; $E - V_3 = I_3 \cdot r$. Oops!

How is possible to solve a mathematical system of tree linear equations to obtain two unknowns? The magic may come from statistics: for shore the recorded values contain little error in, and thus to obtain an 'exact' solution is only a chimera (see Figure 6) since some of the measurements may contain much error in than others (and thus being subject to be outliers).

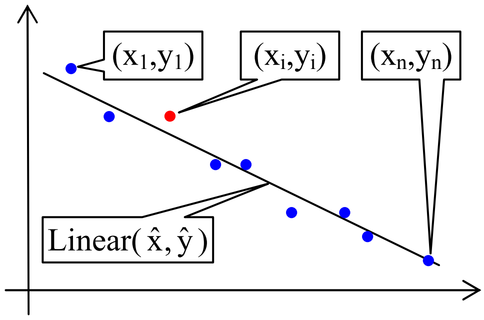


Figure 6. Linear regression challenge

There are many approaches to solve the linear regression, but what is important to remember is that in our case both variables (voltage and current) are subject to errors (see [248], [249], [250]).

One possible approach is to take the values pair by pair and to calculate the unknowns and after that to average the results. Calculation is to be filled in Table 4.

Experiment	Pair	Voltages		Intensities		r	E	Avg(r)	Avg(E)
		V_A	V_B	I_A	I_B	$(V_A-V_B)/(I_B-I_A)$	$V_A+I_A \cdot r$	$(r_{(1,2)}+r_{(1,3)}+r_{(2,3)})/3$	$(E_{(1,2)}+E_{(1,3)}+E_{(2,3)})/3$
Daniell's cell	(1,2)								
	(1,3)								
	(2,3)								
…									

Table 4. Structure of the data analysis results

Further reading

Other papers dealing with regression between measured variables which may be consulted are: [251], [252], [253], [254], [255], [256], [257], [258], [259], [260] and [261].

When the available software does not provide the desired procedure of calculation, the alternative is to build up the calculation procedure by using calculation libraries of generic software (see [262], [263], [264]).

Safety precautions in the laboratory

Introduction

Before starting activity in the laboratory it is necessary to know safe practices that must be followed all times. It is expected to read these rules thoroughly and to pass an exam before beginning the lab work in chemistry.

Purpose

Recognition of laboratory safety and health problems has crystallized since the passage of the Occupational Safety and Health Act of 1970 [265]. Safety and health considerations are as important as any other materials taught in curricula. Occupational studies indicate that the injury rate is highest during the initial period of engagement and decreases with experience. In a laboratory where students experience new activities, the likelihood of incidents, injury, and damage is high. Therefore, it is essential that the students are taught what can go wrong, how to prevent such events from occurring, and what to do in case of an emergency.

General safety measures

When experiments require and the working procedure indicates, approved safety eye glasses or goggles must be worn at all times. There is usually not an increased risk of chemical exposure if you choose to wear contact lenses. The most common exceptions to this are isopropyl alcohol vapours, ethyl alcohol vapours, methylene chloride, and ethylene oxide.

If anything gets in your eye, the eyelids should be held open while flushing the eye with water from the eyewash for 15 minutes. The first 10 seconds are crucial. Immediately go to the nearest eye wash station (at sinks or in the front safety station) and begin flushing the eye. Someone should notify the instructor. Chemical burn hazards, especially hazardous to the eye are concentrated acids and bases, bromine, aluminium chloride and ammonium sulphide.

If there is an accident or injury in the lab, take the appropriate safety measures immediately and then notify the instructor. If there is a large chemical spill on the clothing, the safety shower should be used immediately. Clothing should be removed promptly in the case of a large chemical spill. Wash any chemical off on the skin with water. If your clothing catches on fire, lie down and roll. Someone will bring the fire blanket to you. Please do not run to the blanket or safety shower. Simply smothering it with a sufficiently large watch glass or inverted beaker can put out a small, contained fire. In the case of a multi-neck flask, loosely insert rubber stoppers or corks. Never use a towel - it may overturn the container and spread the fire as well as catch fire itself.

To extinguish an open fire in the laboratory, discharge the small fire extinguishers in the lab.

Discharge at the base or source of the flames, slowly moving from one side to the other to avoid flashback, while calling for assistance and for the sounding of local alarms, if necessary. If the fire is not brought under control and begins to spread, have the fire department called while using the larger extinguisher in the hall. Evacuate everyone from the lab except those involved in extinguishing the fire.

Handling of chemicals

Some solvents are flammable and require precautions concerning there use. Three common extremely flammable solvents are diethyl ether, petroleum ether, and carbon disulfide. All flames and spark sources (motors and heaters) must be turned off in the area that is used for the solvent. A hood must be used for transferring or working with any amount of flammable solvent.

Five common less dangerous, but still highly flammable solvents are acetone, benzene, cyclohexane, ethanol, and methanol. All flame and spark sources in their immediate area should be turned off and a hood should be used for everything except washing glassware. The vapours of all of the above solvents are harmful and should not be inhaled.

In order to prevent respiratory hazards, the following chemicals should be used in the hood only: ammonium hydroxide, concentrated acids (such as nitric, acetic, sulphuric, and hydrochloric acids), ammonium sulphide, acetaldehyde, acetic anhydride, and aniline.

Although will not be attempted to work with explosive hazards in the lab, their existence and potential danger should be known. Organic compounds may react violently with the following substances: ammonium nitrate, potassium chlorate, dichromate ion, permanganate ion, sulphur, perchlorate ion. Solid compounds of silver or mercury as well as oxalates of heavy metals are explosive. Iodine combined with ammonia or aluminium is an explosive reaction.

Bioaccumulants are cumulative poisons, substances that can accumulate in the body and cause health problems. Avoid breathing the dust of these substances. Never dispose of these substances or solutions containing these substances in the drain. Special waste containers will be provided. Cumulative poisons include, but are not limited to, compounds containing one of these elements or ions: silver, lead, antimony, arsenic, beryllium, mercury, cadmium, chromate, dichromate, fluoride.

In the case of liquid mercury, the most likely source is a broken thermometer. It is important that you notify the instructor of any broken thermometers so that special equipment can be used to clean up the spill.

A hood is used to draw toxic or flammable vapours from the laboratory. If are doubts about the efficiency of the hood, the instructor should be asked (to test the airflow). The hood should be used in the case of any doubts about the reaction or toxicity of the compound in use or being produced.

Common sense safety rules

Please follow the next rules:

- Never taste chemicals;
- Do not breathe vapours directly and waft the odour toward your nose instead;
- Treat a test tube with contents that you are heating like a loaded gun and thus never point it in anyone's direction, heat gently along the side and never fill more than half full;
- When pouring liquid chemicals, use a stirring rod to direct the flow;
- Flush sink drains with water after disposing of chemicals there;
- Never return unused solutions of chemicals to the container reagent bottle;
- Add one reagent to another cautiously and slowly;
- Do not add any solid to a liquid over another near to the boiling point of one of them or when the difference of the temperatures is high;
- Please avoid to use mouth suction to fill pipettes;
- Do not use glassware with broken or chipped edges
- When using glass tubing, all ends should be fire polished; to insert glass tubing or rods or thermometers into rubber stoppers, be sure you have the proper size, lubricate the glass with water or glycerine, wrap a towel around the glass, hold the glass near to (less than 5 cm) the rubber stopper, and insert using pressure on the stopper;
- Discard broken glassware in the special glassware collection container and do not discard paper waste with chemical waste;
- Do not store reagents or chemicals in lockers unless you are specifically directed by the instructor to do so;
- Do not use ice from the laboratory ice machine for beverages;
- Long hair, beards, and neckties can be dangerous in the lab because they can catch fire, get into chemicals, or get caught in apparatus, and therefore secure hair and beard out of the way and remove any neckties or scarves;
- Do not wear flared or loose hanging sleeves or scarves; Sandals are not acceptable shoes for lab work and cotton clothing (e.g.; jeans) is safer than polyester.

General behaviour

When conducting laboratory works, please take into consideration that:

- Horseplay or other acts of carelessness are prohibited; do not engage in practical jokes or boisterous conduct in the laboratory and never run in the laboratory;
- The use of personal audio or video equipment is prohibited in the laboratory;

- Keeping your work space neat and clean is a matter of survival;
- Never work alone in the laboratory;
- Reagents and equipment items should be returned to their proper place after use;
- Recipients containing reagents, solutions, glassware shall not be stored for long-term in hoods;
- All containers must be labelled identifying its contents, otherwise should not be used;
- Unauthorized experiments are not permissible because students can not be certain that an experiment is safe to perform; please be aware that infractions of this rule will result in severe academic penalties;
- Chemicals may not be removed from the laboratory because most chemicals are dangerous, particularly under non-laboratory conditions; in any event, unauthorized removal is illegal;
- Because of the risk of getting toxic chemicals into your mouth, you are not permitted to smoke, chew, eat, or drink while in the laboratory;
- Please inform the instructor if you have any physical condition that might present a problem (for example, allergies, epilepsy, breathing disorders, pregnancy);
- Do not perform any experiment while under the influence of drugs or alcohol; besides the obvious danger of this, the vapours of some chemicals are toxic when combined with alcohol in the blood (especially carbon tetrachloride);
- Never leave experiments while in progress and never attempt to catch a falling object;
- Be careful when handling hot glassware and apparatus in the laboratory, because hot glassware looks just like cold glassware;
- Make sure no flammable solvents are in the surrounding area when lighting a flame and do not leave lit Bunsen burners unattended;
- Coats, bags, and other personal items must be stored in designated area near to the laboratory door, not on the bench tops or in the aisle ways and keep the working area neat and free of any unnecessary objects;
- Thoroughly clean your laboratory work space at the end of the laboratory session;

Hygiene practices

Please keep your hands away from your face, eyes, mouth, and body while using chemicals. Food and drink, open or closed, should never be brought into the laboratory or chemical storage area. Do not apply cosmetics while in the laboratory or storage area. Wash the hands after removing gloves, and before leaving the laboratory.

Legal provisions in labour safety

National regulations on the subject are (in force on March 20, 2015 [266]):

- Law 319/2006 - Law on safety and health at work, published in the Romanian Official Gazette, part I, no. 646 from July 26, 2006;
- Law 90/1996 - Labour Protection Law, republished in the Romanian Official Gazette, part I, no. 47 from January 29, 2001;
- Government Decision 1425/2006 approving the Methodological Norms for the application of Law 319/2006 for labour safety, published in the Romanian Official Gazette, part I, no. 882 from October 30, 2006;
- Government Decision 955/2010 amending and supplementing the Norms for the application of Law 319/2006 for labour safety, published in the Romanian Official Gazette, part I, no. 661 from September 27, 2010;
- Law 53/2003 - Labour Code, updated and republished in the Romanian Official Gazette, part I, no. 345 from May 18, 2011;
- Law 108/1999 for the establishment and organization of the labour inspection, republished in the Romanian Official Gazette, part I, no. 740 from October 10, 2002;
- Government Emergency Ordinance 96/2003 on maternity protection at workplaces updated and approved by Law 25/2004, published in the Romanian Official Gazette, part I, no. 214 from March 11, 2004;
- Law 245/2004 on general product safety, republished in the Romanian Official Gazette, part I, no. 899 from December 28, 2007;
- Law 240/2004 on producer responsibility for damages caused by defective products, republished in the Romanian Official Gazette, part I, no. 313 from April 22, 2008;
- Law 436/2001 for approving the Government Emergency Ordinance 99/2000 on measures that can be applied during periods of extreme temperatures to protect the employees', published in the Romanian Official Gazette, part I, no. 404 from July 20, 2001;
- Law 202/2002 on equal opportunities between women and men, republished in the Romanian Official Gazette, part I, no. 150 from March 1, 2007;
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- Law 211/2011 about the regime of the wastes, republished in the Romanian Official Gazette, part I, no. 220 from March 28, 2014;
- Law 360/2003 on dangerous substances and preparations, published in the Romanian Official Gazette, part I, no. 635 from September 5, 2003, and modified by the law 263/2005, published in the Romanian Official Gazette, part I, no. 899 from October 7, 2005;
- Law 451/2001 for approving the Government Emergency Ordinance 200/2000 on classification, labelling and packaging of substances and chemical preparations, published in the Romanian Official Gazette, part I, no. 416 from July 26, 2001.

Student's obligations for conducting experiments in the laboratory

Laboratory of chemistry takes place during the first semester having 7 meetings of conducting laboratory activities. Each student will have a laboratory notebook for recording experimental observations, processing and interpretation of results; laboratory notebook has the following structure:

- ÷ Name, surname, discipline (first page);
- ÷ List of laboratory works and bibliography (second page);
- ÷ Instrumentation Laboratory - drawings and chemical formulas (pages 3 to 5);
- ÷ Successive series of works which will and/or were made (following pages).

Tables of experimental observations, formulas, and tables processing results are compulsory to be in the notebook before the meet for conducting of the each practical activity.

Each student will prepare (you know) the working procedure(s) of the activity planned to be conducted in the laboratory.

Data processing and interpretation of the results are mandatory after conducting of each experiment.

Practical activities are carried out as follows:

1. Presentation of the chemistry laboratory (during the first and second week of the semester). Safety measures in the laboratory are assumed. It is conducted a demonstrative experiment: *Study gaseous diffusion and molecular velocities*. Each student will record (individually) the observed values and will perform all the calculations (same rule applies for the rest of the lab activities).
2. At this point the notebooks must be up to date (during the third and fourth week of the semester). It is conducted a frontal experiment: *Obtaining of the oxygen: study of the gases laws*. At this moment students will be divided into working groups (of 2 to 5 students) for the next series of activities which will be in a cycle (rotation; 3 → 4; 4 → 5; 5 → 6; 6 → 7; 7 → 3).

For the following activities these are planned and conducted in the assigned working group:

3. Activity to be conducted: *Qualitative analysis of metals and alloys*. In this (third) meeting exercises of writing chemical formulas will be conducted too.
4. Activity to be conducted: *Study of chemical reactions*. In this (fourth) meeting tests of writing chemical formulas will be given.
5. Activity to be conducted: *Water analysis*. In this (fifth) meeting tests of writing chemical formulas will be given.
6. Activity to be conducted: *Volumetric and gravimetric methods in study of corrosion*. In this (penultimate) meeting, quizzes tests from laboratory activities will be given.
7. Activity to be conducted: *Nickel corrosion protective electroplating.* In this (ultimate) meeting, quizzes tests from laboratory activities will be given. Laboratory notebooks will be checked.

Laboratory activities are all mandatory and should be conducted according to the schedule. All absences will be recovered. An absence (1/7) is recovered without charge. Recoveries extra charge (from 2/7 to 7/7) must be planned in advance with the supervisor.

Laboratory activity is recorded with admitted/rejected. In order to pass the chemistry laboratory, each student must attend and conduct all 7 laboratory activities and to pass both tests (of chemical formulas and of quizzes from laboratory activities).

Possible bonuses may be archived doing supplementary activities in the laboratory on a voluntary basis. These require knowing of the working procedure and are possible only after approval of the supervisor:

- Conducting the measurements with the *Analytical balance* (for all groups);
- *Producing electricity from electrochemical cells* (to be conducted supplementary in any of the meetings from the second one to the last one);

At the moment of the examination date (planned date for the exam of Chemistry) is required that each student to have given at least once the test from theory on the computer (in the presence of a supervisor). For further details, please visit http://l.academicdirect.org and consult the following works: [267], [268], [269], [270], [271], [272], [273] and [64].

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