# General and Inorganic Chemistry – Laboratory Techniques and Calculations

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**“Development of digital learning materials**
**for renewable pharmaceutical practice-oriented skills**
**in English and Hungarian.**
**Preparing university lecturers for educational challenges of the 21$^{st}$ century.”**
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# Preface

Knowledge of students on Chemistry at the beginning of their graduate studies is rather different. Most of the students do not have proper laboratory expertise. This educational experience prompted the faculty of the institute to compile an educational material that can help students to make themselves familiar with the most important laboratory utensils and perform some basic laboratory processes that are essential for their further studies. The experiments and demonstrations described in the material are preceded by a short introduction of the given topic. This part of the booklet, however, is not intended to give as a detailed description as it is demonstrated by the lectures of the subject. The educational material involves 130 calculation problems that also help a better understanding of the particular topics.

The experiments in this text are designed for a first-year general chemistry course. Selection of the topics somehow reflects that the editors are involved in education of general chemistry for first year Pharmacy students. This course serves as a basis for education of other Chemistry-based subjects among which Pharmaceutical Chemistry is the most important of the Pharmacy curriculum. The educational goal of this integrated subject is introduction to molecular features and structural activity relationships of selected groups of active pharmaceutical ingredients and Pharmacopoeial analysis of selected inorganic and organic substances. This specialty of educational aim of the curriculum is reflected in selection of topics of the course and the present educational material.

The editors express their special thank to Professor Gábor Lente (University of Debrecen, Hungary) for his valuable comments and suggestions to improve the quality of the present educational material, which was intended to compile a reliable electronic form of basics of Chemistry for student at the beginning of their studies.

The module structure of the educational material provides the possibility to introduce new topics, new experiments, demonstrations and calculation problems in the future. Suggestions in relation to such extensions are welcome by the editors. Similarly, the editors are pleased to accept any proposal that improve the text.

March 31, 2014

The editors

# I Chemical nomenclature

The primary aim of chemical nomenclature is to provide methodology for assigning descriptors (names and formulae) to chemical species so that they can be identified without ambiguity.

The first level of nomenclature, beyond the assignment of totally trivial names, gives some systemic information about the substance but does not allow the inference composition (e.g., sulphuric acid, perchloric acid).

When a name itself allows the inference of the stoichiometric formula of a compound according to general rules, it becomes truly systemic. Only a name of this kind of nomenclature becomes suitable for retrieval purposes.

The first systematic nomenclature of inorganic compounds was developed by Guyton's system was extended by the contributions of Lavoisier, Berthollet and de Fourcoy.

When the atomic theory developed to the point where it was possible to write specific formulae for the various oxides and their binary compounds, names reflecting composition more or less accurately then became common. As a number of inorganic compounds rapidly grew, the essential pattern of nomenclature was little altered until near the end of the 19th century.

In 1892 a conference in Geneva laid the basis for an internationally accepted system of organic nomenclature, but at that time there was nothing comparable for inorganic nomenclature. Thus, many ad hoc systems had developed for particular rather than general purposes („*Geneva nomenclature*”).

The need for uniform practice was recognized about the end of the 19th century. In 1921, the International Union of Pure and Applied Chemistry (IUPAC) appointed commissions on the nomenclature of inorganic, organic and biological chemistry. The first comprehensive report („*the Red Book*”) of the inorganic commission was issued in 1940 followed by revisions in 1958 and 1971. In 1990 the IUPAC recommendations were again fully revised in order to bring together the various changes which occurred in the previous years. The committees continue their work to this day.

Since the Geneva nomenclature is still in use for some inorganic compounds, this chapter introduces both nomenclature systems.

## I.1 Classification of matter

All materials, such as air, water, rocks, as well as plant and animal substances consist of matter. *Matter* is the general term for the material things around us and may be defined as whatever occupies space and has mass. All things we can see, touch or use are made of matter.

A material by its chemical constitution is either a *substance* or a *mixture*. A substance is a homogeneous material consisting of one particular kind of matter. A mixture is a material that can be separated by physical means into two or more substances.

A *substance* is a kind of matter that cannot be separated into other kinds of matter by any physical process. Substances can be classified into two classes. These are *elements* (e.g., hydrogen and oxygen) and c*ompounds* (e.g., water). We can transform elements into compounds with chemical change (reactions). A chemical change, or chemical reaction, is a change in which different substances with new properties are formed.

*Mixtures* can also be classified into two types. They are homogeneous and heterogeneous mixture. *Heterogeneous mixtures* are mixtures that consist of physically distinct parts with different properties. Salt and sand (or sand and water) that have been stirred together comprise a heterogeneous mixture.

*Homogeneous mixtures* (also known as *solutions*) are mixtures that are uniform in their properties throughout. When sodium chloride or sugar is dissolved in water, we obtain a homogeneous mixture, or solution. Air is a gaseous solution, principally of two elementary substances, nitrogen and oxygen, which are physically mixed but not chemically combined.

A *chemical change*, or *chemical reaction*, is a change in which one or more kinds of matter are transformed into a new kind of matter or several new kinds of matter. Chemical reactions may involve the formation of compounds from elemental substances. Complex substances may be broken down into simpler compounds or into the constituent elements. Compounds may react with other compounds or elements to form new and different substances. For example, elementary zinc reacts with hydrochloric acid to yield zinc chloride and hydrogen gas.

## I.2 Elements

*Elements* are substances that cannot be further decomposed by ordinary chemical means. An element is composed of the same kind of atoms.

Each element has its own set of properties. General similarities among the properties of large groups of elements provide one way of classifying them. In this sense, elements can be classified as metals, metalloids and non-metals.

An *atom* is the smallest individual structure of an element that retains the properties of the element. It is the smallest unit of an element which can exist either alone or in combination with atoms of the same or different elements.

An atom consists of two basic kinds of particles, a *nucleus* and one or more *electrons*. The nucleus is the central core of an atom; it has most of the mass of the atom and one or more units of positive charge. Nuclei are very small and very dense. They have diameters of about $10^{-15}$ m ($10^{-5}$ Å), whereas atomic diameters are about $10^{-10}$ m (1Å) - a hundred thousand times larger. (1 angstrom (Å) = $10^{-10}$ m.)

Atomic nuclei are composed of two kinds of particles, *protons* and *neutrons*. A *proton* is one of the nuclear particles having a unit positive charge and a mass over 1800 times that of the electron. A *neutron* is another particle found in the nucleus; it has a mass almost identical to that of the proton but has no electrical charge.

The other part of an atom lies outside the central nucleus. It is called *electron cloud*. The electron cloud gives an atom its volume and keeps out other atoms. The electron cloud is made up of electrons. An electron is a very light, pointlike particle having a unit negative electric charge.

All the atoms of one element have the same number of protons. Atoms of different elements have different number of protons, for example carbon atoms have 6 protons while oxygen atoms have 8 protons. The number of protons in an atom tells us which element the atom belongs to. It is called the *atomic number* and has the symbol Z. The atomic number of an element is the number of protons in each atom of the element. The atomic number is written as a subscript number in front of the symbol of the atoms.

Because most of the mass of an atom is in the nucleus, and because protons and neutrons have about the same mass, the total mass of an atom is approximately proportional to the total number of protons and neutrons in the nucleus. The total number of protons and neutrons of an atom is called the *mass number* of the atom. The mass number of an atom is frequently written as a superscript number in front of the symbol of the atom.

The *atomic number* of an atom characterizes an element, which always consists of the same atomic number. A pure element can, however, have atoms with the same numbers of protons (that is, with the same atomic number) but different numbers of neutrons. In such a case all atoms of an element have the same atomic number but they have different mass numbers because the number of neutrons varies.

Thus one form of carbon atoms has a mass number of 12 (6 protons and 6 neutrons) and another has a mass number of 13 (6 protons and 7 neutrons). They are called carbon-12 and carbon-13, respectively. Atoms of the same element having the same number of protons but different numbers of neutrons, such as carbon-12 and carbon-13, are known as *isotopes*. In other words, isotopes are atoms with the same atomic number but different mass numbers.

The names (and the symbols) of isotopes of an element are the same but those of hydrogen, where

| **Mass number** | **Name** | **Symbol** |
|---|---|---|
| 1 | protium | $^1H$ or H |
| 2 | deuterium | $^2H$ or D |
| 3 | tritium | $^3H$ or T |

Isotopes have the same number of electrons and hence the same chemical properties, because chemical properties depend upon the transfer and redistribution of electrons. But isotopes have different numbers of neutrons, so they have different masses and hence different physical properties.

A naturally occurring element consists of either a single isotope (as in the case of sodium, which contains only sodium-23) or a definite mixture of two or more isotopes. Table I-1 shows a list of natural isotopes of some of the elements.

**Table I-1:** Isotopic distribution of some naturally occurring elements

| **Element** | **Mass number of isotope** | **Abundance (%)** |
|---|---|---|
| Hydrogen | $^1H$ | 99.985 |
| | $^2H$ | 0.015 |
| | $^3H$ | $10^{-10}$ |
| Oxygen | $^{16}O$ | 99.759 |
| | $^{17}O$ | 0.037 |
| | $^{18}O$ | 0.204 |
| Carbon | $^{12}C$ | 98.892 |
| | $^{13}C$ | 1.108 |
| | $^{14}C$ | 0.000 000 000 1 |

## I.3 Compounds

Most substances are *compounds*. A compound is a substance composed of more than one element, which are chemically combined.

Each compound has an *empirical formula* containing the symbols of the elements in it. The empirical formula of a compound is a notation that uses atomic symbols with numerical subscripts to express the relative proportions of atoms of the different elements in the compound. For example, carbon dioxide has the formula $CO_2$, which means that the compound is composed of carbon atoms and oxygen atoms in the ratio 1 to 2.

Additional information may be conveyed by different kinds of chemical formulas. To understand this, we need to look briefly at the two main types of substances: molecular and ionic.

A *molecular substance* is a substance that is composed of molecules all of which are alike (e.g., water, $H_2O$; ammonia, $NH_3$; carbon dioxide, $CO_2$).

A *molecule* is a definite group of atoms that are chemically bonded together. A molecular formula is a chemical formula that gives the exact number of different atoms of an element in a molecule. The water molecule contains two hydrogen atoms and one oxygen atom chemically bonded. Therefore its molecular formula is $H_2O$. Other examples of molecular substances are: ammonia, $NH_3$; carbon dioxide, $CO_2$; and methanol, $CH_3OH$.

Some elementary substances are molecular in nature and are represented by molecular formulas. Chlorine, for example, is a molecular substance and has the formula $Cl_2$. Other examples are hydrogen ($H_2$), nitrogen ($N_2$), oxygen ($O_2$), fluorine ($F_2$), phosphorous ($P_4$), sulphur ($S_8$), bromine ($Br_2$) and iodine ($I_2$).

The atoms in a molecule are bonded together in a definite way. A *structural formula* is a chemical formula that shows how the atoms are bonded to one another in a molecule. For example, the structural formula of water is H-O-H. A line joining two atomic symbols in such a formula represents the chemical bond connecting the atoms.

Although many substances are molecular, others are composed of ions. An *ion* is an electrically charged particle obtained from an atom or chemically bonded group of atoms by adding or removing electrons.

An *ionic compound* is a compound composed of cations and anions. Sodium chloride, for example, consists of equal number of sodium ions, $Na^+$, and chloride ions, $Cl^-$. The strong electrostatic attraction between positive and negative charges holds the ions together in a regular arrangement in space. Such a regular arrangement gives rise to a crystal, a kind of solid having a definite geometrical shape as a result of the regular arrangement of the ions making up the substance.

The formula of an ionic compound expresses the lowest possible whole-number ratio of different ions in the substance, except that the charges on the ions are omitted. For example, sodium chloride contains equal numbers of $Na^+$ and $Cl^-$ ions. The formula, that is called empirical formula, is written NaCl (not $Na^+Cl^-$).

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## I.4 Naming compounds

The empirical formula of a compound expresses the stoichiometric composition, *the lowest possible whole-number ratio of different atoms in the substance.* For compounds composed of individual molecules the empirical formula corresponding to the relative molecular mass should be used. (e.g. $S_2Cl_2$ and $H_4P_2O_6$ not SCl or $H_2PO_3$.) If the relative molecular mass changes (e.g. due to thermal dissociation), the simplest formula is used (e.g., S, P, $NO_2$ not $S_8$, $P_4$, $N_2O_4$), except if we want to emphasize the presence of the polymeric modification. The formula of atomic lattice (e.g., $SiO_2$) or ionic (such as NaCl, $CaCl_2$) compounds only expresses the ratio of the number of atoms (ions) in the substance.

If the compound contains more than one electropositive (cation) or electronegative (anion) component, the atoms within each group are listed *in alphabetical order* of their chemical symbols made. $NH_4$ ion should be considered as a two-letter symbol, so it is listed after Na. Hydrogen is an exception to this rule, because the acidic hydrogen is listed among the cations last.
For example:

| | |
|---|---|
| $KMgF_3$ | potassium magnesium fluoride |
| $KHCO_3$ | potassium hydrogen carbonate |
| $MgNH_4PO_4.6\ H_2O$ | magnesium ammonium phosphate-water (1/6) |
| $NaNH_4HPO_4$ | sodium ammonium hydrogen phosphate |
| $KLiNaPO_4$ | potassium lithium sodium phosphate |

Simple covalent compounds are generally named by using prefixes to indicate how many atoms of each element are shown in the formula. The prefixes are Greek numbers as follows: 1=*mono*, 2=*di*, 3=*tri*, 4=*tetra*, 5=*penta*, 6=*hexa*, 7=*hepta*, 8=*octa*, 9=*ennea* (or *nona*), 10=*deca*. When number of atoms is too high or unknown, the *poly*-prefix is used. Half is noted by *semi*-, one and a half with the *sesqui*- prefixes.

In case of compounds containing more than one anions the order of the anions in the formula is as follows:

a. $H^-$, $O^{2-}$, $OH^-$
b. The other monatomic inorganic anions (other than $H^-$ and $O^{2-}$) are listed in the following the order: Rn, Xe, Kr, B, Si, C, Sb, As, P, F, Te, Se, S, A, I , Br, Cl, O, F.
c. Polyatomic inorganic anions (excluding $OH^-$) are listed according to their increasing number of atoms, while those with the same number of atoms according to the descending order of atomic number of the central ions (e.g., $CO_3^{2-}$, $CrO_4^{2-}$, $CrO_4^{2-}$, $SO_4^{2-}$).
d. Organic anions are listed in alphabetical order.

In the name of compounds consisting of two non-metallic elements should be written in the order mentioned under b.) with addition that hydrogen is in the line between the N and Te. For example, $NH_3$, $H_2S$, $CCl_4$, $ClO_2$, $OF_2$.

When naming covalent molecules consisting of two different non-metal atoms, use the following steps:

a. The first (more electropositive) atom in the name, give the first name of the molecule. A Greek prefix is used to show the number of atoms. "*Mono*" is not used to name the first element.

b. The second (more electronegative) atom in the name has a Greek prefix showing the number of atoms followed by the name which ends in *-ide*.

For example:

| | |
|---|---|
| $NO_2$ | nitrogen dioxide |
| $N_2O$ | dinitrogen oxide |
| $N_2O_5$ | dinitrogen pentoxide |
| $SF_6$ | sulphur hexafluoride |

Latin or Greek multiplier names (*bis-*, *tris-*, *tetrakis-*, etc..) are used in the following cases:

a. when the name of group of atoms contains a number. For example, bisdisulphide, bistriphosphate,
b. before complex names (the name of which the multiplier name refers, is in brackets). For example, bis (hydrogen sulphide).

When a compound contains three or more electropositive or electronegative elements, the order generally follows the sequence related to the connection of the atoms in the molecule. For example, HOCN: cyanic acid, HNCO: isocyanic acid. Some common formulae (e.g., $H_2SO_4$, $HClO_4$, $HNO_3$) do not match this rule, but - because of their ubiquity - this order can be maintained. The number of the same atoms or groups in the formula is indicated by Arabic numerals. The number is placed in the lower right of the symbol or that of the parenthesis of the complex ion, as an index. The number of water molecules of crystallization and that of the loosely bound molecules are placed in front of their formula indicated by Arabic numerals. For example, $CaCl_2 \cdot 8H_2O$, $Na_2SO_4 \cdot 10\ H_2O$.

## I.4.1 Naming ions

### I.4.1.1 Naming cations

a. **Monoatomic cations**

The simplest ions are monoatomic ions. A monoatomic ion *is an ion formed from a single atom*. Metallic elements generally form monoatomic cations. Nonmetal elements generally form monoatomic anions.

*A* monoatomic cation *is given the name of the element*. If there is more than one cation of the element with different oxidation states (e.g., iron, which has the $Fe^{2+}$ and $Fe^{3+}$) the charge is denoted by a Roman numeral in parentheses immediately following the element's name. The ion $Fe^{2+}$ is called iron(II) ion.

For example:

| | | | |
|---|---|---|---|
| $Fe^{2+}$ | iron(II) ion | or | iron(2+) ion |
| $Sn^{4+}$ | tin(IV) ion | or | tin(4+) ion |
| $Ni^{3+}$ | nickel(III) ion | or | nickel(3+) ion |

b. **Polyatomic cations**

The name of cations that are formed by combination of a hydrogen ion and a hydride of an element of the halogen-, oxygen- or the nitrogen-group is formed by adding the suffix „*-onium*” to the root of the name of the element: the name of $H_4N^+$ is *ammonium*, that of $H_3O^+$ is *oxonium*, and that of $H_2F^+$ is *fluoronium*. Ammonium is used instead nitronium, because the latter is widely used for naming the $NO_2^+$ cation.

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The name of polyatomic cations (*acyl groups*) obtained by (imaginary) removal of a *hydroxyl group* from an acid is obtained from the full or a stem name of the non-metallic element followed by the suffix -*yl*.

For example:

| | |
|---|---|
| $IO_2^+$ | iodyl |
| $SO^{2+}$ | thionyl |
| $SO_2^{2+}$ | sulphuryl |
| $CO^{2+}$ | carbonyl |
| $PO^{3+}$ | phosphoryl |
| $NO^+$ | nitrosyl (nitrosonium) |
| $NO_2^+$ | nitryl (nitronium) |

### I.4.1.2 Naming anions

a. The names of **monoatomic anions** are obtained from a stem name of the element followed by the suffix -ide.

For example:

| | |
|---|---|
| $H^-$ | hydr*ide* ion |
| $Cl^-$ | chlor*ide* ion |
| $F^-$ | fluor*ide* ion |
| $S^{2-}$ | sulp*hide* ion |
| $N^{3-}$ | nitr*ide* ion |
| $C^{4-}$ | carb*ide* ion |
| $O^{2-}$ | ox*ide* ion |

b. *A* **polyatomic ion** *is an ion consisting of two or more atoms chemically bonded together and carrying a net electric charge*. The names of polyatomic anions are obtained from a full name, or stem name, or the Latin name of the central element followed by the suffix *–ate*. In the first part of the name of the anion, the name(s) of the other element(s) – which are listed in the formula following the central element – is (are) named according to the following rules: Greek prefixes are used to designate the number of each type of atom followed by the full name, or stem name or Latin name of the atom(s) followed by the suffix *–o* (e.g., *oxo*- for oxygen, *thio*- for sulphur, etc.). In case of multivalent central atoms the oxidation state of the atom is given as a Roman numeral in parentheses, following the name of the atom.

For example:

| **Formula** | **IUPAC nomenclature** | **Geneva nomenclature** |
|---|---|---|
| $SO_4^{2-}$ | tetraoxosulphate(VI) | sulphate |
| $NO_2^-$ | dioxonitrate(III) | nitrate |
| $PO_4^{3-}$ | tetraoxophosphate(V) | phosphate |
| $S_2O_3^{2}$ | trioxothiosulphate(VI) | thiosulphate |
| $ClO_2^-$ | dioxochlorate(III) | chlorite |
| $ClO_3^-$ | trioxochlorate(V) | chlorate |

Many of the polyatomic ions are *oxyanions*, which consist of oxygen with another element (called the central element). If the central atom of the oxyanion can form ions with different number of oxygen atoms they can be distinguished by suffixes added to the stem name of the element.

The suffix -*ite* denotes the anion with the fewer number of oxygen atoms; the suffix -*ate* denotes the anion with the greater number of oxygen atoms. For example, $SO_3^{2-}$ - is the sulp*hite* ion, and $SO_4^{2-}$ is the sulp*hate* ion.

The formula and the name (Geneva nomenclature) of the most frequently occurring oxyanions are listed in Table I-2.

**Table I-2:** The formula and the name (Geneva nomenclature) of the most frequently occurring oxyanions

| Name | Formula | Name | Formula |
|---|---|---|---|
| Ammonium | $NH_4^+$ | Nitrite | $NO_2^-$ |
| Carbonate | $CO_3^{2-}$ | Nitrate | $NO_3^-$ |
| Hydrogen carbonate | $HCO_3^-$ | Sulphite | $SO_3^{2-}$ |
| Hydroxide | $OH^-$ | Hydrogen sulphite | $HSO_3^-$ |
| Hypochlorite | $ClO^-$ | Sulphate | $SO_4^{2-}$ |
| Chlorite | $ClO_2^-$ | Hydrogen sulphate | $HSO_4^-$ |
| Chlorate | $ClO_3^-$ | Phosphate | $PO_4^{3-}$ |
| Perchlorate | $ClO_4^-$ | Hydrogen phosphate | $HPO_4^{2-}$ |
| Cyanide | $CN^-$ | Dihydrogen phosphate | $H_2PO_4^-$ |

When there are several oxyanions of a given central element, they can be distinguished by adding prefixes. The oxyanion with the greatest number of oxygen atoms is given the prefix *per*- and the suffix -*ate*. The oxyanion with the least number of oxygen atoms is given the prefix *hypo*- and the suffix *ate*-.

For example:

| | |
|---|---|
| $ClO^-$ | *hypo*chlor*ite* ion |
| $ClO_2^-$ | chlor*ite* ion |
| $ClO_3^-$ | chlor*ate* ion |
| $ClO_4^-$ | *per*chlor*ate* ion |

*Acid anions* are anions that have H atoms they can lose as hydrogen ion, H+. For example, $HSO_4^-$ (derived from $H_2SO_4$) has an H atom that can be removed to yield H+ and $SO_4^{2-}$. The acid anion, $HSO_4^-$, is called *hydrogen sulphate ion*.

### I.4.2 Naming acids

*Acids* are substances that yield hydrogen ions (protons), $H^+$, in aqueous solution. An *oxyacid* is an acid that donate protons in aqueous solution previously were bonded to oxygen atoms. Today the Geneva nomenclature is still widely used for naming acids and their salts.

The name of the oxygen-containing acids (oxyacid's) is formed from the name of the oxyanion by replacing the suffix *-ite* by *-ous,* and the suffix *-ate* by *-ic*, then adding the word *acid.*
For example

| **Oxyanion** | | **Oxyacid** | |
|---|---|---|---|
| $SO_3^{2-}$ | sulp*hite* ion | $H_2SO_3$ | sulphu*rous* acid |
| $SO_4^{2-}$ | sulp*hate* ion | $H_2SO_4$ | sulphu*ric* acid |
| $ClO_2^-$ | chlor*ite* ion | $HClO_2$ | chlor*ous* acid |
| $ClO_3^-$ | chlor*ate* ion | $HClO_3$ | chlor*ic* acid |
| $NO_2^-$ | nitr*ite* ion | $HNO_2$ | nitr*ous* acid |
| $NO_3^-$ | nitr*ate* ion | $HNO_3$ | nitr*ic* acid |
| $CO_3^{2-}$ | carbon*ate* ion | $H_2CO_3$ | carbon*ic* acid |

The aqueous (acidic) solutions of binary compounds of hydrogen and non-metals (e.g., HCl and HBr) we name like compounds by using the prefix *hydro*- and the suffix -*ic* with the stem name of the non-metal, followed by the name of the word *acid.*

For example:

| | |
|---|---|
| HCl(*aq*) | *hydro*chlor*ic acid* |
| HBr(*aq*) | *hydro*brom*ic acid* |
| HI(*aq*) | *hydro*iodic *acid* |

In the names of widely used salts - when the name unambiguously expresses the formula of the salt - the stoichiometric ratios are not necessarily indicated.

For example:

| | |
|---|---|
| $Na_2SO_4$ | sodium sulphate |
| $NaHSO_3$ | sodium hydrogen sulphite |
| NaOCl | sodium hypochlorite |
| $KIO_4$ | potassium periodate |

In trivial names it is the *peroxy*- prefix which indicates replacement of (-O-) with (-OO-).

For example:

| | |
|---|---|
| $H_2SO_5$ | peroxysulfuric acid |
| $H_2S_2O_8$ | peroxydisulfuric acid |

While naming thioacids, the *thio*- prefix should be added before the name of the oxyacid, from which the thioacid was formed by replacing oxygen with sulphur. The number of sulphur atoms should be indicated by Greek numbers.

For example:

| | |
|---|---|
| $H_2S_2O_3$ | thiosulphuric acid |
| $H_3PO_3S$ | monothiophosphoric acid |
| $H_3PO_2S_2$ | dithiophosphoric acid |
| $H_2CS_3$ | trithiocarbonic acid |

### I.4.3 Naming functional derivatives of acids

*Functional derivatives of acids* are compounds derived from oxyacids by replacing a hydroxyl group (sometimes an O-atom) with another atom or group of atoms.

*Acid halides* (also known as *acyl halides*) are compounds derived from oxyacids by replacing a hydroxyl group with a halide group. The names of acid halides are formed by adding the name of the halide to the name of the acyl group.

For example:

| | |
|---|---|
| $NOCl$ | nitrosyl chloride |
| $NO_2Br$ | nitryl bromide |
| $POI_3$ | phosphoryl iodide |
| $COCl_2$ | carbonyl chloride (phosgene) |
| $CrO_2Cl_2$ | chromyl chloride |

*Acid amides* are compounds derived from oxyacids by replacing a hydroxyl group with an amino (or substituted amino) group. The names of acid amides are formed by adding the word *amide* to the name of the acyl group.

For example:

| | |
|---|---|
| $SO_2(NH_2)_2$ | sulphonyl diamide |
| $PO(NH_2)_3$ | phosphoryl triamide |
| $CO(NH_2)_2$ | carbonyl diamide (carbamide) |

When any of the hydroxyl groups of a polyprotic acid is not replaced with amino group, the name is formed by adding the *amido*- prefix to the name of the acid.

For example:

| | |
|---|---|
| $NH_2SO_3H$ | amidosulphuric acid |
| $NH_2CO_2H$ | amidocarbonic acid (carbamic acid) |

Regarding naming, esters of the inorganic acids should be considered as salts.

For example:

| | |
|---|---|
| $(CH_3)_2SO_4$ | dimethyl sulphate |
| $(C_2H_5)_3BO_3$ | triethyl borate |

### I.4.4 Naming bases

**Bases** *are substances that yield hydroxide ions, OH-, in aqueous solution*. Inorganic bases are usually ionic and are named as ionic compounds.

For example:

| | |
|---|---|
| $NaOH$ | sodium hydroxide |
| $NH_4OH$ | ammonium hydroxide |
| $Ca(OH)_2$ | calcium hydroxide |
| $Fe(OH)_2$ | iron(II) hydroxide |

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## I.4.5 Coordination compounds

A *complex* is a substance in which a metal atom or ion is associated with a group of neutral molecules or anions called ligands. *Coordination compounds* are neutral substances (i.e. uncharged) in which at least one ion is present as a complex.

To name a coordination compound, no matter whether the complex ion is the cation or the anion, *always name the cation before the anion*. (This is just like naming an ionic compound.)

The formula of the complex group is enclosed in square brackets. The order of the constituents of the complex group as it follows: *central atom* (or ion), *ionic ligands, neutral ligands* (water, ammonia). The ion as well as the neutral molecules should be listed in alphabetical order.

### I.4.5.1 Naming ligands

a. The name of the neutral ligand remains unchanged with the following exceptions: water ($H_2O$) – aqua, ammonia ($NH_3$) – ammin, nitrogen monoxide (NO) – nitroso, and carbon monoxide (CO) – carbonyl.

| **Formula** | **Name of molecule** | **Name of ligand** |
|---|---|---|
| $H_2O$ | water | aqua |
| $NH_3$ | ammonia | ammin |
| NO | nitrogen monoxide | nitroso |
| CO | carbon monoxide | carbonyl |

b. The names of anionic ligands are obtained from the full or the stem name of the anion followed by the suffix *–o.*

| **Formula** | **Name of molecule** | **Name of ligand** |
|---|---|---|
| $H^-$ | hydride | hydrido |
| $S^{2-}$ | sulphide | thio |
| $F^-$ | fluoride | fluoro |
| $Cl^-$ | chloride | chloro |
| $O^{2-}$ | oxide | oxo |
| $OH^-$ | hydroxide | hydroxo |
| $CN^-$ | cyanide | cyano |
| $SCN^-$ | thiocyanate | thiocyano |
| $NO_2^-$ | nitrite | nitrito or nitro (depending on the nature of the bonding atom) |

### I.4.5.2 Naming complex compounds

To name a coordination compound, no matter whether the complex ion is the cation or the anion, *always name the cation before the anion*. (This is just like naming an ionic compound.).

In naming complex ions the ligand(s) is(are) named first and the central ion (atom) second. The complete ligand name consists of a Greek prefix denoting the number of ligands, followed by the specific name of the ligand. Regardless the number and the charge of each, the ligands are named in alphabetical order (disregarding Greek prefixes).

a. In name of complex cations and neutral complexes the central metal ion (atom) is named as the element. In case of multivalent metal ions the oxidation state of the metal in the complex is given as a Roman numeral in parentheses, following the name of the metal.
   Greek prefixes are used to designate the number of each type of ligand in the complex ion, e.g. *di-*, *tri-* and *tetra-*. If the ligand already contains a Greek prefix (e.g. ethylene*di*amine) or if it is polydentate ligands (i.e. can attach at more than one binding site) the prefixes *bis-*, *tris-*, *tetrakis-*, *pentakis-*, are used instead.

For example:

| | |
|---|---|
| $[Cu(NH_3)_4]SO_4$ | tetraammincopper(II) sulphate |
| $[Al(OH)(H_2O)_5]Cl_2$ | pentaaquahydoxoaluminium(III) chloride |
| $[Fe(SCN)(H_2O)_5]Cl_2$ | pentaaquathiocyanoiron(III) chloride |
| $[Fe(SCN)_2[H_2O)_4]Cl$ | [tetraaquabis(thiocyano)iron(III) chloride |
| $[Fe(CO)_4]$ | tetracarbonyliron(0) |
| $[Pt(NH_3)_2Cl_2]$ | diammindichloroplatinum(II) |

b. In name of complex anions the name of the central metal ion (atom) consists of the name of the metal followed by the suffix *–ate*. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses. For some metals, the Latin names are used in the complex anions e.g. Fe is called ferrate (not ironate).

For example:

| | |
|---|---|
| $K_4[Fe(CN)_6]$ | potassiumhexacyanoferrate(II) |
| $[Cr(NH_3)_3(H_2O)_3]Cl_3$ | triamminetriaquachromium(III) chloride |
| $[Pt(NH_3)_5Cl]Br_3$ | pentaamminechloroplatinum(IV) bromide |
| $Na_2[NiCl_4]$ | sodium tetrachloronickelate(II) |
| $Pt(NH_3)_2Cl_4$ | diamminetetrachloroplatinum(IV) |
| $K_4[Fe(CN)_6]$ | potassiumhexacyanoferrate(II) |
| $Na_3[Ag(S_2O_3)_2]$ | sodium bis(thioszulfato)argentate(I) |
| $K_2[Cd(CN)_4]$ | potassium tetracyanocadmiate(II) |
| $Na[BiI_4]$ | sodium tetraiodobismutate(III) |
| $K[Sb(OH)_6]$ | potassium hexahidroxoantimonate(V) |
| $Na_2[Ni(CN)_2Br_2]$ | sodium dibromodicianonickelate(II) |

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## I.4.6 Addition compounds

### I.4.6.1 Formula of addition compounds

An addition compound contains two or more simpler compounds that can be packed in a definite ratio into a crystal. A dot is used to separate the compounds in the formula. For example, $CuSO_4 \cdot 5\ H_2O$ is an addition compound of copper sulphate and water.

### I.4.6.2 Naming addition compounds

In name of addition compounds the names of components are linked by a hyphen. The number of the molecules is indicated by Arabic numbers, separated by a slash.

For example:

| | |
|---|---|
| $Na_2CO_3 \cdot 10\ H_2O$ | sodium carbonate-water(l/10) |
| $3\ CdSO_4 \cdot 8\ H_2O$ | cadmium sulphate-water (3/8) |
| $8\ Kr \cdot 46\ H_2O$ | krypton-water (8/46) |
| $CaCl_2 \cdot 8\ NH_3$ | calcium chloride-ammonia (1/8) |
| $Al_2Ca_4O_7 \cdot nH_2O$ | dialuminium tetracalcium heptoxyde-water (l/n) |

## I.4.7 Practice problems

**Give the following compounds name!**

a. $NaHCO_3$
b. $KAl(SO_4)_2$
c. $K_2HPO_4$
d. $Fe_2(SO_4)_3$
e. $Ca(H_2PO_3)_2$
f. $CaCl(OCl)$
g. $Ca_3(AsO_4)_2$
h. $Ca[SiF_6]$
i. $(NH_4)_2CrO_4$
j. $Na_2HAsO_3$
k. $Sb_2S_3$
l. $[PtCl_2(NH_3)_2]$
m. $[Co(NO_2)_2(NH_3)_4]Cl$
n. $K_3[Fe(CN)_6]$
o. $Ba[BrF_4]_2$
p. $[CoCl_2(H_2O)_4]Cl$
q. $Na_2[Fe(CN)_5(NO)]$
r. $Cu[(NH_3)_4(H_2O)_2]SO_4$
s. $[Ni(NH_3)_6]SO_4$
t. $Ni(CO)_4$

**Write down the empirical formula or molecular formula of the following compounds**

a.) phosphorous(V) oxide
b.) barium trioxocarbonate (IV)
c.) carbon disulphide
d.) silicon tetrafluoride
e.) tetramethyl silane
f.) cobalt(II) tetrakis(thiocyanato)mercurate(II)
g.) potassium dibromodiiodomercurate(II)
h.) sodium hexacyanoferrate(II)
i.) calcium tetraoxophosphate(V)
j.) potassium tetracianonickelate(0)
k.) hexaamminplatinum(IV) sulphate
l.) tetraammindichloroplatinum(IV) chloride
m.) lithium tetrahydroaluminate(III)
n.) barium bis[(dihydrogen)tetraoxooxophosphate(V)]
o.) potassium trioxobromate(V)
p.) sodium tetraoxoarsenate(V)
q.) sodium tetrahydroxoaluminate(III)
r.) hexaaquachrom(III) chloride
s.) sodium diaquatetrahydroxoaluminate(III)
t.) tris(ethylenediamine)cobalt(III) chloride

# II Writing chemical equations

The chemical transformations are described in form of *chemical equations*. Chemical equations express both *qualitative* and *quantitative* relationships between reactants and products. On the left side of chemical equation, the reactants are listed, while on the right side, the products are, separated by an arrow or an equality sign.

## II.1 Qualitative relationships

Only the facts should be described, i.e., reactants really taking part in the reaction and products really formed should be involved in the equation. The first step in writing a correct chemical equation involves describing these basic facts in a word equation.

1. *Word equations*: This verbal equation is a brief statement that gives the names of the chemical species involved in the reaction. Word equations do not give any quantities, thus they have only qualitative significance.
   Experiments show, e. g. that hydrogen can be combusted to form water. The word equation for this reaction is

   hydrogen + oxygen = water

   stating only experimental facts without specifying reaction conditions or relative quantities of the substances.
2. *Skeletal formula equations*: Replacing names by formula sin a word equation, skeletal formula equations may be constructed.

$$2\ H_2 + O_2 = 2\ H_2O$$

Particular attention should be paid to give *correct formulas*. Thus, *elements* existing in the form of *diatomic* covalent molecules should be formulated $X_2$, others should be given in *monoatomic* form (e. g. instead of $S_8$ we write S, instead of $P_4$ we write P, etc.). Formulas of compounds should be given in their simplest atom-to-atom ratios. ($P_2O_5$ instead of $P_4O_{10}$ and $SiO_2$ instead of $Si_nO_{2n}$, etc.). Finally, quantitative relationships should be established, as follows.

## II.2 Quantitative relationships

1. *Balanced formula equations*: The requirements of the *mass-conservation law* can be fulfilled easily in constructing chemical equations. Considering that the mass of the atoms does not change during a chemical reaction, the mass-conservation law appears to the chemical equation as the *law of conservation of atoms*. In other words, a balanced equation should have coefficients so that *the number of all the atomic species on the reactant side is equal to their number on the product side*. Furthermore, the smallest possible coefficients should be given as shown below:

$$2\ H_2 + O_2 = 2\ H_2O \qquad \text{(balanced equation),}$$

and not $4\ H_2 + 2O_2 = 4\ H_2O$

Additional information can be noted in an equation referring to *reaction conditions, state of matter, catalyst or heat effect*.

Examples:

1. State of matter emphasized:

$$2\ H_{2\ (g)} + O_{2\ (g)} = 2\ H_2O_{\ (g)}$$

$$\text{or } 2\ H_{2\ (g)} + O_{2\ (g)} = 2\ H_2O_{\ (l)}$$

$$\text{or } 2\ H_{2\ (g)} + O_{2\ (g)} = 2\ H_2O_{\ (s)}$$

2. Reaction conditions emphasized:

$$2\ H_2O_{2\ (l)} \xrightarrow[25°C]{Pt} 2\ H_2O_{(g)} + O_{2(g)}$$

3. Heat effect noted:

$$3\ H_{2\ (g)} + N_{2\ (g)} \leftrightarrow 2\ NH_{3\ (g)} \qquad \Delta H = -92\ kJ$$

(In the latter case it is necessary to note the state of matter because phase transformations influence the heat effects.)

The most widely used forms of balanced chemical equations are the so-called *stoichiometric equations* and *ionic equations*.

*Stoichiometric equations* comprise formulas of *compounds*. It is advantageous to use this type of equations when the equation serves for stoichiometric calculations. For example, the interaction of hydrochloric acid solution and silver nitrate solution to yield silver chloride precipitate can be written as follows:

$$HCl_{(aq)} + AgNO_{3(aq)} = AgCl_{(s)} + HNO_{3(aq)},$$

when the purpose is to calculate the relative amounts of the reactants required to produce a given amount of silver chloride.

*Ionic equations* are preferred mostly for describing chemical reactions occurring in aqueous solutions in which the dissolved substances (acids, bases, salts) are present in (partially or totally) dissociated form. In most cases, the following types of aqueous reactions are described in this way:

a. precipitate formation or the reverse reaction
b. gas formation
c. acid-base reactions
d. reactions in which water-soluble, non-dissociating covalent compounds form
e. complex-forming reactions, ions involved.

When constructing ionic equations, in addition to the aforementioned rules, *the rule of charge conservation* is to be considered, i.e., the sum of the electric charges should be equal on both sides of the ionic equation.

The following example demonstrates the way of constructing an ionic equation, according to the precipitate formation from hydrochloric acid and silver nitrate solutions. The stoichiometric equation comprises the formulas of *compounds* being reacted and formed, but the state of the *particles* involved in the process in neglected.

Hydrochloric acid, silver nitrate and nitric acid exist in ionized (dissociated) form in an aqueous solution.

The stoichiometric equation:

$$HCl_{(aq)} + AgNO_{3(aq)} = AgCl_{(s)} + HNO_{3(aq)}$$

Concerning the *existing* particles:

$$H^{+}_{(aq)} + Cl^{-}_{(aq)} + Ag^{+}_{(aq)} + NO_3{}^{-}_{(aq)} = AgCl_{(s)} + H^{+}_{(aq)} + NO_3{}^{-}_{(aq)}$$

It can be seen that the $H^{+}_{(aq)}$ and $NO_3{}^{-}_{(aq)}$ ions do not take part in the precipitate formation (they are so-called *spectator ions*). Therefore, these two can be omitted form the equation.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} = AgCl_{(s)}$$

Further simplification can be made omitting the note „(*aq*)” and underlining the formula of the precipitate:

Charges:

$$\overset{1+}{Ag^{+}} + \overset{1-}{Cl^{-}} = \overset{\text{no charge}}{\underline{AgCl}}$$

Description of a gas formation (e.g. the interaction of sodium carbonate and hydrochloric acid solutions) in the form of a stoichiometric equation is a misinterpretation of the chemical change:

$$Na_2CO_3 + 2\ HCl = 2\ NaCl + H_2O + CO_2$$

Considering the state of the participants:

$$2\ Na^{+} + CO_3^{2-} + 2\ H^{+} + 2\ Cl^{-} = 2\ Na^{+} + 2\ Cl^{-} + H_2O + CO_2$$

Omitting the spectator ions:

$$CO_3^{2-} + 2\ H^{+} = H_2O + CO_2$$

All the *aqueous reactions* of strong acids with strong bases should be considered as ion reactions in which hydrogen ions and hydroxide ions form non-dissociated water molecules, disregarding the spectator counterions, e.g.:

$$2\ Na^{+} + 2\ OH^{-} + 2\ H^{+} + SO_4^{2-} = 2\ H_2O + 2\ Na^{+} + SO_4^{2-}$$

After the usual simplification:

$$H^{+} + OH^{-} = H_2O$$

The reaction of *Brønsted acids and bases* is described as a *proton-transfer reaction*:

$$NH_4^{+} + H_2O \rightleftharpoons NH_3 + H_3O^{+}$$

There are ionic reactions in which non-dissociated, water-soluble molecules are formed. Then, the equation is written as follows:

$$Fe^{3+}{}_{(aq)} + 3\ SCN^{-}{}_{(aq)} = Fe(SCN)_{3(aq)}$$

| $Fe^{3+}$ | + | $3\ SCN^{-}$ | = | $Fe(SCN)_3$ |
|---|---|---|---|---|
| pale yellow | | colourless | | red |

Ionic complex-formation reactions can be written in the usual way. However, it is necessary to know the *coordination number* of the metal ion (the number of the directly attached ions or molecules). If one knows that the coordination number of iron(II) ion is 6, the complex ion formation of the former with $CN^-$ ions can be written as follows:

$$Fe^{2+}{}_{(aq)} + 6\ CN^{-}{}_{(aq)} = [Fe(CN)_6]^{4-}{}_{(aq)}$$

or $$Fe^{2+} + 6\ CN^{-} = [Fe(CN)_6]^{4-}$$

The complex compounds are usually well-soluble in water:

$$K_4[Fe(CN)_6] = 4\ K^{+} + [Fe(CN)_6]^{4-}$$

The entity in square brackets (the complex ion) does not dissociate in water.

## II.3 Writing redox reactions

*Redox reactions* involve an *electron transfer* from one particle onto another. *Oxidation means a half-reaction in which a substance (atomic, ionic or molecular) releases electron(s). In the reduction half-reaction electron(s) is/are accepted.* Thus, oxidation and reduction are antiparallel and simultaneously occurring electron-transfer processes. The two opposite processes can be separated in space (see chapter IX). In organic and biochemical reactions oxidation is frequently accompanied by gaining oxygen or loosing hydrogen atoms; while reduction is manifested as loosing oxygen or gaining hydrogen atoms.

As regard redox reactions, the most important characteristic of the participants in the *oxidation number* of atoms. The oxidation number is defined as the *existing or assigned electric charge of a particle* calculated as follows:

a. Ions have an oxidation number equal to their free charge.
b. Polyatomic particles are arbitrarily dissected into monoatomic particles, and the electron pairs of the covalent bonds are assigned to the more electronegative atom. The number of these hypothetical charges of the „ion" formed by this fiction is the assigned oxidation number of the constituent atom of the molecule or the polyatomic ion. The sum of the hypothetical charges is equal to the charge of the polyatomic particle.

The latter method of calculating oxidation numbers requires, of course, the prior knowledge of the covalent bonding system of the polyatomic particle. Fortunately, simple rules derived from this method can be used to calculate oxidation numbers directly from formulas. The most important rules as follows.

Rule 1. Atoms in elementary state have an oxidation number of *zero* ($N_2$, $Cl_2$).
Rule 2. The oxidation number of monoatomic ions is the *free charge* of the ion.

Rule 3. In polyatomic particles, the covalent bonds between two identical atoms are neglected, e.g.:

$$\overset{+1}{H} – \overset{-1}{O} – \overset{-1}{O} - \overset{+1}{H}$$

Rule 4. The oxidation number of oxygen is usually -2 except in peroxy compounds (-1), in superoxides (-1/2) and in compounds fluorine with oxygen (+2).
Rule 5. The oxidation number of hydrogen is usually +1 except in metal hydrides where it is -1 (e.g. in $AlH_3$).
Rule 6. The oxidation number of metals is usually *positive.*

There are cases when an atom has more than one oxidation number is molecule, e.g. nitrogen atoms in dinitrogen oxide.

$$\overset{0}{N} = \overset{+2}{N} = \overset{-2}{O}$$

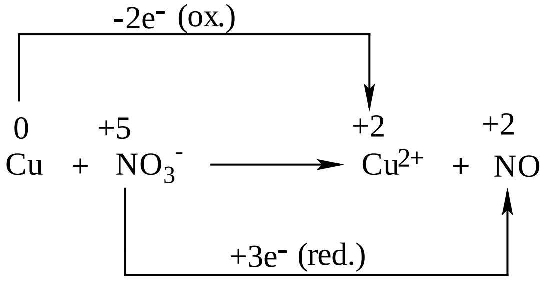
In such cases, instead of operating with the 0 and +2 individual oxidation numbers, one can calculate with the *average oxidation number* +1 for both nitrogen atoms.

Examples:

Dissolution of elementary copper in dilute nitric acid. The easiest way to obtain a balanced chemical equation is the use of oxidation numbers in the following way:

Step 1. The oxidation states of the starting materials and those of the products are determined.

$$\overset{0}{Cu} + \overset{+5\ -2}{NO_3^-} \rightarrow \overset{+2}{Cu^{2+}} + \overset{+2\ -2}{NO}$$



Step 2. The changes in the oxidation states are determined: Copper losing two electrons is oxidized, and the nitrate ion gaining 3 electrons is reduced.

Step 3. Only an equal number of electrons may take part in the two half-reactions (i.e. may be transferred). This is *the smallest common multiple* of 2 and 3 ($2 \cdot 3 = 3 \cdot 2 = 6$). Thus, the appropriate coefficients are:

$$3\ Cu + 2\ NO_3^- \rightarrow 3\ Cu^{2+} + 2\ NO$$

Step 4. Finally, the oxygen balance should be established. Of the 6 oxygen atoms on the left, 2 atoms have formed nitrogen monoxide. The rest will combine with 8 hydrogen ions to form 4 moles of water in a non-redox process.

$$2\,\overset{+1}{H}{}^{+} + \overset{-2}{O_2}{}^{-} = \overset{+1\,-2}{H_2O}$$

The complete and balanced equation can be seen below:

$$3\,Cu + 8\,H^{+} + 2\,NO_3^{-} = 3\,Cu^{2+} + 2\,NO + 4\,H_2O$$

Specific redox processes are the *disproportionation* and *synproportionation* reactions. *Disproportionation* reactions are redox processes in which a single starting material of an intermediate oxidation state forms both a more oxidized and a reduced product, (i.e. one particle oxidizes another particle of the same substance, while the former one is reduced). The reverse reaction type is called *synproportionation*, when two substances of different oxidation state react to form a single substance of the same intermediate oxidation state.

The reaction of elementary chlorine with sodium hydroxide is a *disproportionation reaction*:

$$\overset{0}{Cl_2} + 2\,NaOH \rightarrow Na\overset{-1}{Cl} + NaO\overset{+1}{Cl} + H_2O$$

For determining the coefficients it is advisable to write an ionic equation:

$$Cl_2 + 2\,OH^{-} \rightarrow Cl^{-} + OCl^{-} + H_2O$$

Oxidation number of one of the chlorine atoms of the chlorine molecule is reduced and that of the other is increased. One chlorine atom is reduced to chloride ion while the other chlorine atom is oxidized to hypochlorite ion. Both half-reactions involve transfer of one electron:

$$Cl + 1e^{-} \rightarrow Cl^{-}$$
$$Cl - 1e^{-} \rightarrow OCl^{-}$$

The reaction of potassium iodide with potassium iodate in acidic medium is an example of synproportionation:

$$K\overset{-1}{I} + K\overset{+5}{I}O_3 + H_2SO_4 \rightarrow \overset{0}{I_2} + H_2O + K_2SO_4$$

The skeletal ionic equation:

$$IO_3^{-} + I^{-} + H^{+} \rightarrow I_2 + H_2O$$

During the reaction course, iodide ion is oxidized to iodine by losing an electron while iodate ion is reduced to iodine accepting five electrons. It is obvious that to fulfil the five electron demand of the iodate ion, five iodide ions should release five electrons and, as a result, three moles of iodine form:

$$5\,I^{-} + IO_3^{-} + 6\,H^{+} = 3\,I_2 + 3H_2O$$

The stoichiometric equation is as follows:

$$5\,KI + KIO_3 + 3\,H_2SO_4 = 3\,I_2 + 3\,H_2O + 3\,K_2SO_4$$

## II.4 Practice problems

**Balance the following redox equations**

a.) $H_2O_2 + HI = I_2 + H_2O$
b.) $I_2 + Na_2S_2O_3 = NaI + Na_2S_4O_6$
c.) $NaOCl = NaClO_3 + NaCl$
d.) $Br_2 + NaOH = NaBr + NaOBr + H_2O$
e.) $HNO_2 = HNO_3 + NO + H_2O$
f.) $HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$
g.) $K + H_2O = KOH + H_2$
h.) $HCOOH + KMnO_4 = MnO_2 + CO_2 + H_2O + KOH$
i.) $MnO_2 + HBr = MnCl_2 + Br_2 + H_2O$
j.) $Ag + KCN + O_2 + H_2O = K[Ag(CN)_2] + KOH$
k.) $Sn + NaOH + H_2O = Na[Sn(OH)_3] + H_2$
l.) $Pb + PbO_2 + H_2SO_4 = PbSO_4 + H_2O$
m.) $As_2S_3 + NH_3 + H_2O_2 = (NH_4)_3AsO_4 + S + H_2O$
n.) $MnO_2 + KNO_3 + KOH = K_2MnO_4 + KNO_2 + H_2O$
o.) $NH_3 + O_2 = N_2 + H_2O$
p.) $NH_3 + O_2 = NO + H_2O$
q.) $S^{2-} + NO_3^- + H^+ = S_8 + NO_2 + H_2O$
r.) $SO_2 + MnO_4^- + H_2O = SO_4^{2-} + Mn^{2+} + H^+$
s.) $I^- + MnO_4^- + H_2O = IO_3^- + MnO_2 + OH^-$
t.) $MnO_4^- + S^{2-} + H_2O = MnO_2 + S + OH^-$
u.) $KMnO_4 + H_2O_2 + H_2SO_4 = MnSO_4 + K_2SO_4 + H_2O + O_2$
v.) $KMnO_4 + FeSO_4 + H_2SO_4 = MnSO_4 + K_2SO_4 + Fe_2(SO_4)_3 + H_2O$
w.) $K_2Cr_2O_7 + KI + H_2SO_4 = Cr_2(SO_4)_3 + I_2 + K_2SO_4 + H_2O$
x.) $FeCl_3 + KI = I_2 + FeCl_2 + KCl$
y.) $I_2 + SO_3^{2-} + H_2O = I^- + SO_4^{2-} + H^+$

# III Basic laboratory procedures and methods

## III.1 Basic guidelines for working with hazardous materials

### III.1.1 Laboratory safety

When working in a chemical laboratory we are handling several chemicals with more or less adverse effects to human health, and we are performing experiments that have number of potential hazards associated with them. Thus, a chemical laboratory can be a dangerous place to work in. With proper care and circumspection, strictly following all precautionary measures, however, practically all accidents can be prevented!

It is the prevention of accidents and damages posed by the specialty of the chemical laboratory experiments that requires you to follow the instructor's advice as well as keep the laboratory order during work in the laboratory. You should never forget that your carelessness or negligence can threaten not only your own safety but that of your classmates working around you!

This section has guidelines that are essential to perform your experiments is s safe way without accident.

#### III.1.1.1 Preparation in advance

a) *Read through the descriptions of the experiments carefully!* If necessary, do study the theoretical background of the experiments from your textbook(s). After understanding, write down the outline of the experiments to be performed in your laboratory notebook. If any items you don't understand remain, do ask your instructor before starting work.
b) *Prepare your notebook before the laboratory practice!* Besides description of the outline of the experiments, preliminary preparation should also include a list of the before starting work.

#### III.1.1.2 Laboratory rules

a) The laboratory instructor is the first to enter and the last to leave the laboratory. Before the instructor's arrival students must not enter the laboratory.
b) Always wear laboratory coat and shoes in the laboratory. Sandals and open-toed shoes offer inadequate protection against spilled chemicals or broken glass.
c) Always maintain a disciplined attitude in the laboratory. Careless acts are strictly prohibited. Most of the serious accidents are due to carelessness and negligence.
d) Never undertake any unauthorized experiment or variations of those described in the laboratory manual.
e) Maintain an orderly, clean laboratory desk and cabinet. Immediately clean up all chemical spills from the bench and wipe them off the outer wall of the reagent bottles with a dry cloth.
f) Smoking, drinking, or eating is not permitted during the laboratory practice. Do not bring other belongings than your notebook, stationery, and laboratory manual into the laboratory. Other properties should be placed into the locker at the corridor.
g) Be aware of your neighbours' activities. If necessary, warn them of improper techniques or unsafe manipulation.

h) At the end of the lab, completely clean all glassware and equipment, and clean it with a dry cloth. After putting back all your personal labware into your cabinet, lock it carefully.
i) Always wash your hands with soap before leaving the laboratory.

### III.1.1.3 Handling chemicals and glassware

a) At the beginning of the laboratory practices the instructor holds a short introduction when all questions related to the experimental procedures can be discussed.
b) Perform each experiment alone. During your work always keep your laboratory notebook at hand in order to record the results of the experiments you actually perform.
c) Handle all chemicals used in the experiments with great care. Never taste, smell, or touch a chemical or solution unless specifically directed to do so.
d) Avoid direct contact with all chemicals. Hands contaminated with potentially harmful chemicals may cause severe eye or skin irritations.
e) Reactions involving strong acids, strong bases, or chemicals with unpleasant odour should be performed under the ventilating hood. If necessary, safety glasses or goggles should be worn.
f) When checking the odour of a substance, be careful not to inhale very much of the material. Never hold your nose directly over the container and inhale deeply.
g) When performing an experiment, first and the label on the bottle twice to be sure of using the correct reagent. *The wrong reagent can lead to accidents or "inexplicable" results in your experiments*.
h) Do not use a larger amount of reagents than the experiment calls for. *Do not return any reagent to a reagent bottle!* There is always the chance that you accidentally pour back some foreign substance which may react with the chemical in the bottle in an explosive manner.
i) Do not insert your own pipette, glass rod, or spatula into the reagent bottles; you may introduce impurities which could spoil the experiment for the person using the stock reagent after you.
j) Mix reagents always slowly. Pour concentrated solutions slowly and continuously stirring into water or into a less concentrated solution. *This is especially important when diluting concentrated sulphuric acid*.
k) Discard waste or excess chemicals as directed by your laboratory instructor. The sink is not for the disposal of everything: Solid waste (indicator and filter paper, pumice, granulated metal, etc.) should be placed into the dust bin.
l) Using clean glassware is the basic requirement of any laboratory work. Clean all glassware with a test-tube brush and a detergent, using tap water. Rinse first with tap water and then with distilled water. If dry glassware is needed, dry the wet one in drying oven, or rinse with acetone and air dry it.

## III.1.2 Accident protection, fire protection and first aid

### III.1.2.1 Accident and fire protection

a) Before starting the experiments make sure all the glassware are intact. Do not use cracked or broken glassware. If glassware breaks during the experiment, the chemical spill and the glass splinters should be cleaned up immediately. Damaged glassware should be replaced from the stock laboratory.

b) Fill not more than 4-5 cm$^3$ of reactants into a test-tube. *As you are performing the experiments, do not look into the mouth of the test-tube and do not point it at anyone*. If you want to check the odour of a substance formed in a test-tube reaction, waft the vapours from the mouth of the test-tube toward you with your hand.

c) Before heating glassware make sure that its outer wall is dry. Wet glassware can easily break on heating. When heating liquids in a test-tube, hold it with a piece of tightly folded strip of paper or a test-tube holder.

d) When heating liquids in an Erlenmeyer flask or in a beaker, support the glassware on wire gauze placed on an iron tripod, and put a piece of boiling stone into the liquid to prevent bumping. Start heating with a law flame and intensify it gradually.

e) When lighting the Bunsen burner, close the air-intake holes at the base of the burner, open the gas cock of the outlet, and bring a lighted match to the mouth of the burner tube until the escaping gas at the top ignites. (It is advantageous to strike the match first and then open the gas cock.) After it ignites, adjust the air control until the flame is pale blue and the burner produces a slight buzzing sound.

f) If the Bunsen burner “burns in”, which can be noticed from its green flame and whistling (whizzing) sound, the gas cock of the outlet should be turned off immediately. Allow the burner to cool, and light it again as described above.

g) When using an electric heater or other electric device, do not touch them with wet hands and prevent liquids from spilling over them. If it accidentally happens (e.g. a flask cracks on heating), unplug the device immediately and wipe off the liquid with a dry cloth.

h) As a general rule, a flame should be used to heat only aqueous solution. *When working with flammable organic solvents* (e.g. hexane, diethyl ether, petroleum ether, benzene) *use of any open flame in the laboratory is prohibited!* A hot water bath can be effectively used to heat these solvents. The vapours of the flammable substances may waft for some distance down their source; thus presenting fire danger practically in the whole laboratory.

i) Never blow the fire. This way you might turn the fire up and the flame can shoot into your face. *Do not use water to smother fires caused by water-immiscible chemicals (e.g. benzene) and alkali metals. Pouring water on a plugged electric device is also prohibited.*

j) If your clothing catches fire, you can smother the flames by wrapping yourself in a wet towel or a laboratory coat.

k) In case of a smaller fire (e.g. a few cm$^3$’s of organic solvent burning in a beaker or an Erlenmeyer flask), it can be extinguished by placing a watch glass over the mouth of the flask. In case of a bigger fire and more serious danger, use the fire extinguisher fixed on the wall of the laboratory. At the same time alarm the University Fire Fighter Office by calling the phone number 105 from the corridor or from the stock lab.

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l) In case of fire in the laboratory the main gas cock and the electric switch of the laboratory should be turned off immediately. (They are located in the corridor on the outer wall of the laboratory.) Besides fighting the fire, start giving the injured first aid immediately.

### III.1.2.2 Firs aid

a) In case of an accident or injury, even if it is minor, notify your laboratory instructor at once. The urgent first aid is an absolute for the prevention of more serious adverse health effect.
b) Minor burns caused by flames or contact with hot objects should be cooled immediately by flooding the burned area with cold water, then treating it with an ointment. Serve burns must be examined by a physician.
c) In case of a cut, remove the contamination and the glass splinters from the wound. Disinfect its boundary with alcoholic iodine solution and bind it up with sterile gauze. In case of severe cases the wound should be examined and treated by a physician.
d) Whenever your skin gets into contact with chemicals, wash it quickly and thoroughly with water. In case of chemical burns, the chemical should be neutralized. For acid burns, the application of a *dilute solution of sodium hydrogen carbonate*, for burns by alkali, the application of a *dilute solution of boric acid* is used. After neutralization, wash the affected area with water for 5-10 minutes and apply an appropriate ointment if necessary.
e) *Concentrated sulphuric acid dripped onto your skin must be wiped away with a dry cloth*. Then the affected area should be treated as described for acid burns above.
f) Acids splashed onto your clothes could be neutralized with diluted solution of ammonia or sodium hydrogen carbonate.
g) If any chemical gets into your mouth, spit it out immediately, and wash your mouth well with water.
h) If any chemical enters your eyes, immediately irrigate the eyes with large quantities of water. *In case of any kind of eye damage consult a physician immediately.*
i) In case of inhalation of toxic chemicals the injured should be taken out to fresh air as soon as possible.
j) In case of an electric shock, the immediate cut-off the electric current supply of the laboratory (main switch) is the most important step to avoid irreversible health damage. The injured should get medical attention as soon as possible. If necessary, artificial respiration should be given until the physician arrives.

## III.2 Units of measurements

A *physical quantity* is the product of a numerical value and a unit of measurement. The same physical quantity can be measured by different units of measurements. The International System of Units (Système International d'Unités) is a standard metric system of units adopted for official scientific use. The system has been adopted by most countries in the developed (OECD) world, though within English-speaking countries (e.g., The United Kingdom, The United States), the adoption has not been universal. In everyday life and documents of nonregulatory bodies (e.g. scientific communities) use of non-SI units (e.g. liter, degree Celsius, minute, hour, day, degree, etc.) is still rather common.

There are three classes of SI units:
(a) seven *base units* that are regarded as dimensionally independent;
(b) two *supplementary, dimensionless units* for plane and solid angles; and
(c) *derived units* that are formed by combining base and supplementary units in algebraic expressions; such derived units often have special names and symbols and can be used in forming other derived units.

1. **Base units of the SI system**

   There are seven base units, each representing, by convention, different kinds of physical quantities.

| **Quantity name** | **Quantity symbol** | **Unit name** | **Unit symbol** |
|---|---|---|---|
| length | l (small letter L) | metre | m |
| mass | m | kilogram | kg |
| time | t | second | s |
| electric current | I (capital i) | ampere | A |
| thermodynamic temperature | T | kelvin | K |
| amount of substance | n | mole | mol |
| luminous intensity | $I_v$ | candela | cd |

**Definition of base units of the SI system**

1. The *metre* is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
2. The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
3. The *second* is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium 133 atom.
4. The *ampere* is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 meter apart in vacuum, would produce between these conductors a force equal to $2 \cdot 10^{-7}$ newton per meter of length.
5. The *kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

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6. The *mole* is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12; its symbol is “mol.” When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
7. The *candela* is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \cdot 10^{12}$ hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

## 2. Supplementary units of the SI system

| **Quantity name** | **Quantity symbol** | **Expression in terms of SI base units** | **Unit name** | **Unit symbol** |
|---|---|---|---|---|
| plane angle | $\alpha, \beta, \gamma, \ldots$. | $m \cdot m^{-1}$ | radian | rad |
| solid angle | $\Omega, \omega$ | $m^2 \cdot m^{-2}$ | steradian | sr |

## 3. Derived units of the SI system

*Derived units* are expressed algebraically in terms of base units or other derived units. The symbols for the derived units are obtained by means of the mathematical operations of multiplication and division. For example, the derived unit for the derived quantity molar mass (mass divided by amount of substance) is the kilogram per mole, symbol kg/mol. Some derived units have special names and symbols. For example, the SI unit of frequency is specified as the hertz (Hz) rather than the reciprocal second ($s^{-1}$), and the SI unit of moment of force is specified as the newton meter ($N \cdot m$) rather than the joule (J).

The most important derived units used in the *Pharmacopoeia* as it follows:

| **Quantity name** | **Quantity symbol** | **Expression in terms of SI base units** | **Unit name** | **Unit symbol** |
|---|---|---|---|---|
| Wavenumber | ν | $m^{-1}$ | reciprocal metre | 1/m |
| Wavelength | l | $10^{-6}$ m | micrometre | mm |
| | | $10^{-9}$ m | nanometre | nm |
| Area | A, S | $m^2$ | square metre | $m^2$ |
| Volume | V | $m^3$ | cubic metre | $m^3$ |
| Frequency | ν | $s^{-1}$ | hertz | Hz |
| Density, mass density | ρ | $kg \cdot m^{-3}$ | kilogram/cubic-metre | $kg \cdot m^{-3}$ |
| Force, weight | F | $m \cdot kg \cdot s^{-2}$ | newton | N |
| Pressure, stress | p | $m^{-1} \cdot kg \cdot s^2$ | pascal | Pa |
| Dynamic viscosity | η | $m^{-1} \cdot k \cdot s^{-1}$ | pascal second | Pa·s |
| Kinematic viscosity, diffusion coefficient | ν | $m^2 \cdot s^{-1}$ | square metre/ second | $m^2/s$ |

| **Quantity name** | **Quantity symbol** | **Expression in terms of SI base units** | **Unit name** | **Unit symbol** |
|---|---|---|---|---|
| Voltage, electrical potential difference | U | $m^2 \cdot kgs^{-3} \cdot A^{-1}$ | volt | V |
| Electrical resistance | R | $m^2 \cdot kg \cdot s^{-3} \cdot A^{-2}$ | ohm | Ω |
| Electric charge | Q | $A \cdot s$ | coulomb | C |
| Molar concentration | c | $mol \cdot m^{-3}$ | mole/cubic metre | $mol/m^3$ |
| Mass concentration | ρ | $kg \cdot m^{-3}$ | kilogram/cubic metre | $kg/m^3$ |

## 4. **Decimal multiples and submultiples of SI units: SI prefixes**

The SI *prefixes* are used to form decimal multiples and submultiples of units. The prefix name attached directly to the name of the unit, and a prefix symbol attaches directly to the symbol of a unit.

| **Prefix** | **Factor** | **Symbol** | **Prefix** | **Factor** | **Symbol** |
|---|---|---|---|---|---|
| deci- | $10^{-1}$ | d | deka- | $10^{1}$ | da |
| centi- | $10^{-2}$ | c | hecto- | $10^{2}$ | h |
| milli- | $10^{-3}$ | m | kilo- | $10^{3}$ | k |
| micro- | $10^{-6}$ | µ | mega- | $10^{6}$ | M |
| nano- | $10^{-9}$ | n | giga- | $10^{9}$ | G |
| pico- | $10^{-12}$ | p | tera- | $10^{12}$ | T |
| femto- | $10^{-15}$ | f | peta- | $10^{15}$ | P |

## III.3 Labware

### III.3.1 Laboratory devices

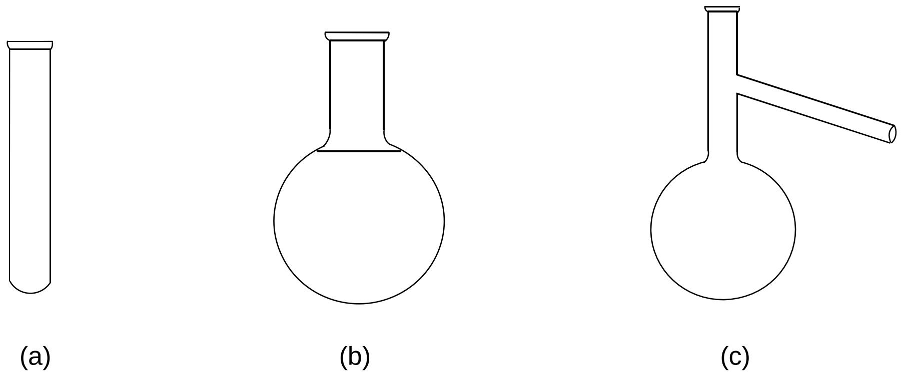
#### III.3.1.1 Laboratory glassware

*Laboratory glassware* refers to a variety of equipment, traditionally made of glass. Glass is an amorphous form of molten $SiO_2$, CaO and $Na_2O$. Laboratory glassware can be classified as thermostable, less thermostable and non-thermostable ware.

##### III.3.1.1.1. Thermostable glassware

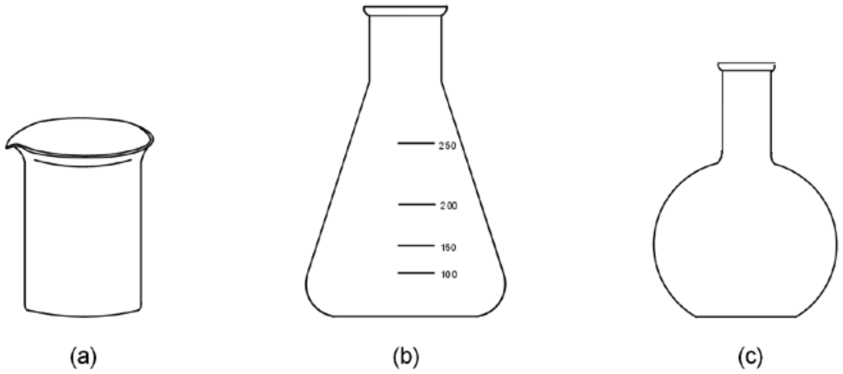
a. **Glassware that can be heated on open fire** (Figure III-1.)
   *test tube* (a), *round bottomed flask* (b), *fractionating flask* (c).
   They are made of glass of low *thermal expansion coefficient* that is why they are more resistant to thermal shock. Heating must be done carefully because thermal expansion in one portion of the glass, but not an adjacent portion, may put too much mechanical stress on the surface and cause it to fracture.

**Figure III-1.** Glassware that can be heated on open fire



b. **Glassware that can be heated on asbestos wire gauze** (Figure III-2.)
   *beaker* (a), *Erlenmeyer-flask* (b), *flat-bottomed* flask (c).
   They are flat-bottomed so that the glass has increased internal pressure. These flasks can be used for boiling and mixing solutions since they can stand alone. They can be heated on asbestos wire gauze or by heating mantle.

**Figure III-2.** Glassware that can be heated on asbestos wire gauze

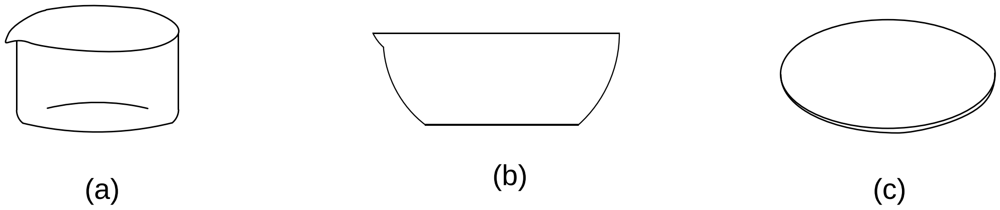


### III.3.1.1.2. **Moderately thermostable glassware** (Figure III-3.)

*crystallization dish* (a), *evaporating dish* (b), *watchglass* (c).

They can only be heated in heated bath. The heated bath is a fluid placed in an open (metal) pot. Water and silicone oil are the most commonly used fluids

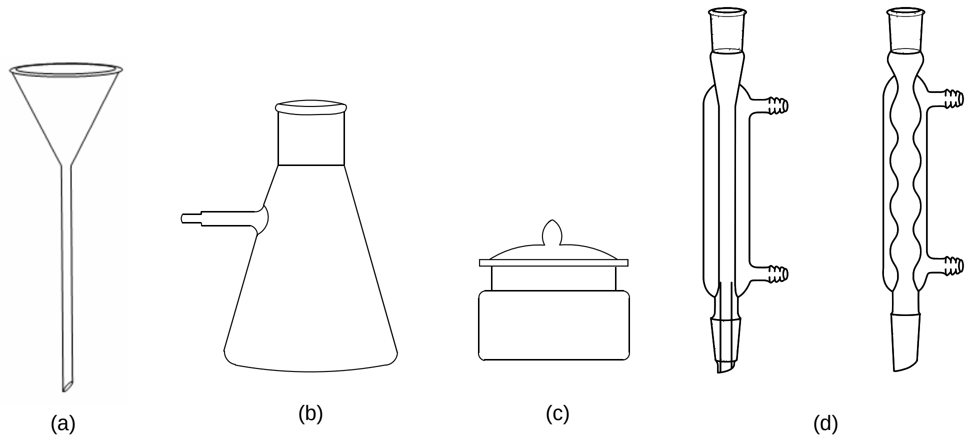
**Figure III-3.** Moderately thermostable glassware


(a) (b) (c)

### III.3.1.1.3. **Non-thermostable glassware** (Figure III-4.)

*glass funnels* (a), *Buchner-flask (vacuum resistant)* (b), *weighing dish* (c), *condensers* (d).

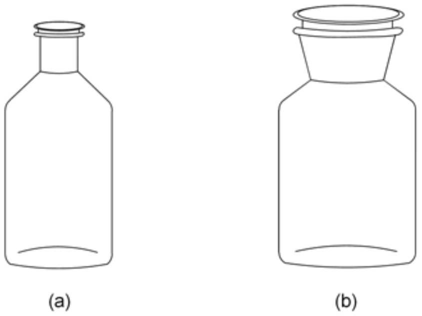
**Figure III-4.** Non-thermostable glassware


(a) (b) (c) (d)

### III.3.1.1.4. **Glassware for storage** (Figure III-5.)

*reagent bottle* (a), *powder jar* (b).

**Figure III-5.** Glassware for storage


(a) (b)

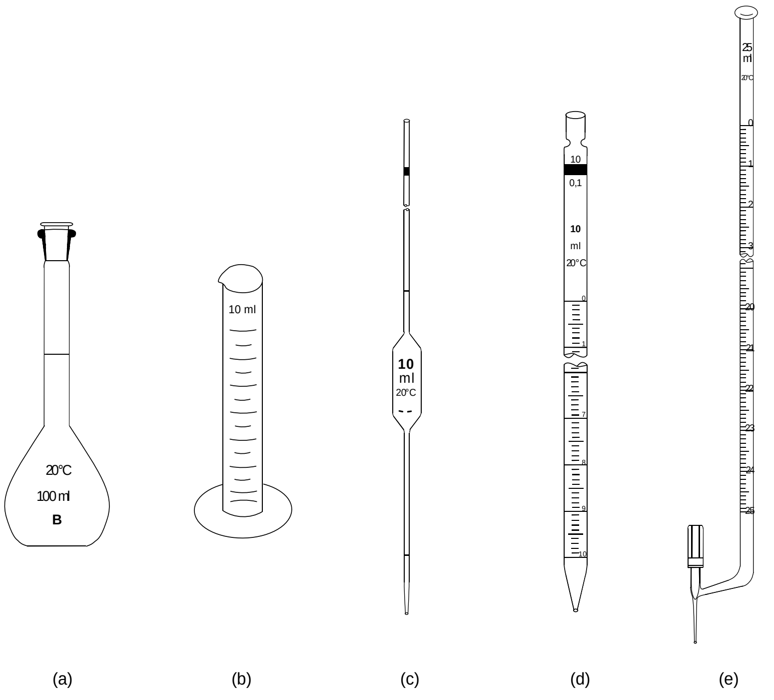
### III.3.1.1.5. Volumetric glassware

Volumetric glassware is specialized pieces of glassware which are used to measure volumes of liquids very precisely in quantitative laboratory work. Each piece of volumetric glassware is marked with its total volume and a temperature (usually 20°C). The marked temperature indicates the temperature at which the apparatus was calibrated. Volumetric glassware should not be heated! (They volume can be irreversibly changed.)

Volumetric glassware can be classified if they are calibrated to contain or to deliver (Figure III-6.).

1. *Glassware calibrated to contain* can contain accurate volume of liquid but that pouring the liquid into another container will not necessarily deliver the indicated volume. The most important ones are the *volumetric flasks* (a) and the *graduated cylinders* (b).
2. Glassware calibrated to deliver is used to accurately deliver or transfer the stated volume to another container. These are the pipettes, (c), the graduated measuring pipettes (d) and the burettes (e).

**Figure III-6.** Volumetric glassware


(a) (b) (c) (d) (e)

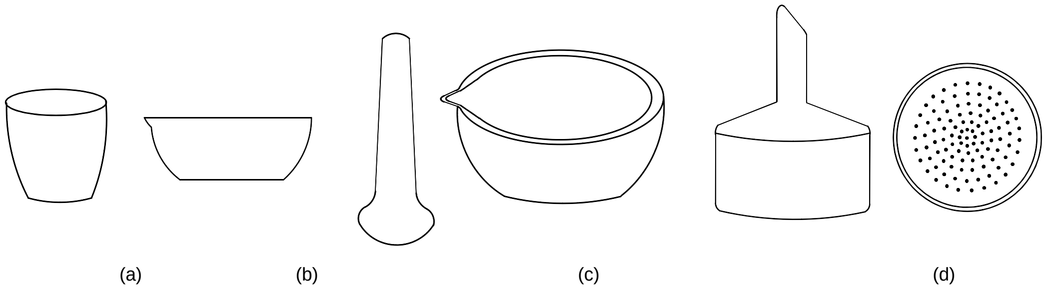
### III.3.1.1.6. **Most important porcelain ware** (Figure III-7.)

Thermostable or non-thermostable laboratory ware made of porcelain

a. **Thermostable porcelain ware**
   *porcelain crucible* (a) – can be heated by open flame or in laboratory ovens; *porcelain dish* (b) – can be heated on asbestos wire gauze or in a heated bath.

b. **Non-thermastable porcelain ware**
   *porcelain mortar* (c) –used for pulverization of solids. *Buchner-funnel* (d) – used for vacuum filtering

**Figure III-7.** Most important porcelain ware

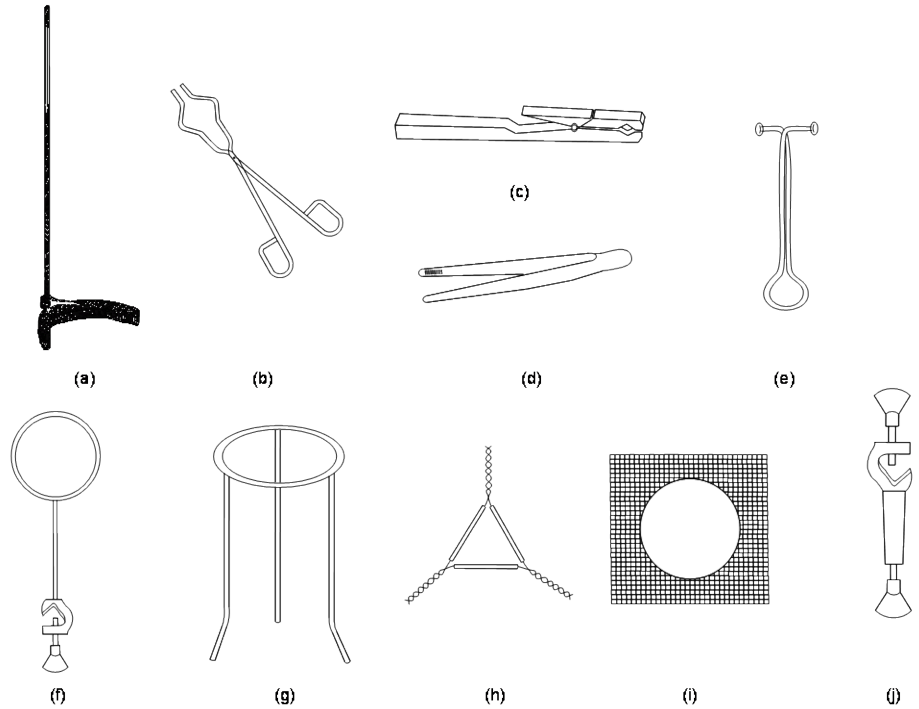


### III.3.1.1.7. **Most important labware made of metal or wood** (Figure III-8.)

These laboratory devices are used to handle or fix various labware

*Bunsen-stand* (a), *crucible tongs* (b), *test tube clamp* (c), *metal tweezers* (d), *Mohr tubing clamps* (e), *funnel holder* (f), *Bunsen tripod* (g), *clay triangle* (h), *asbestos wire gauze* (i), *clamp holder* (j).

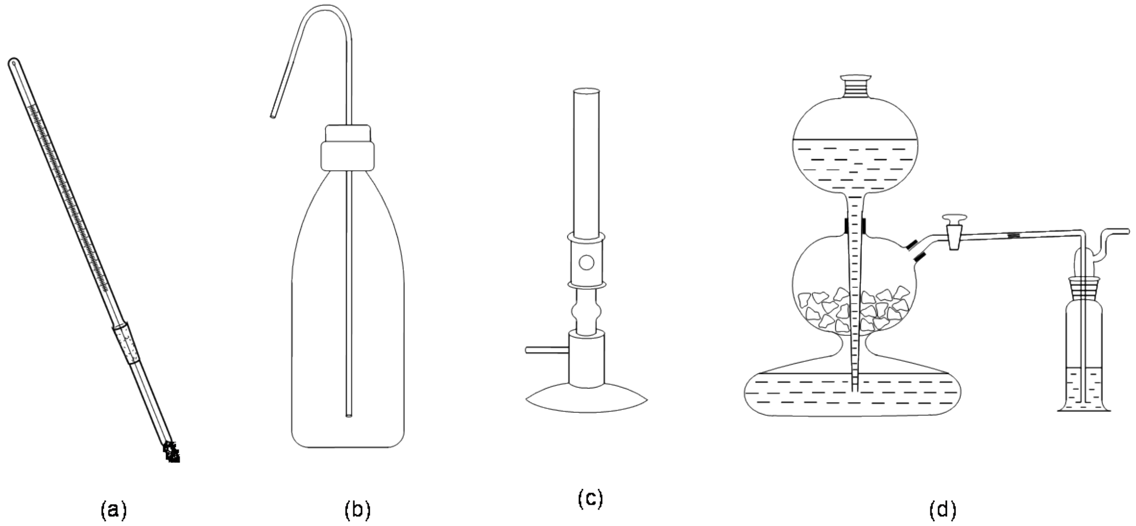
**Figure III-8.** Most important labware made of metal or wood



### III.3.1.1.8. **Other labware** (Figure III-9.)

Other labware frequently used in a chemical laboratory: *thermometers* (a), *wash bottles* (b) and *Bunsen-burner* (c) *Kipp's apparatus*, also called *Kipp generator*, is an apparatus designed for preparation of small volumes of gases (d)

**Figure III-9.** Other labware



## III.3.2 Cleaning of laboratory glassware and porcelain ware

There are many different methods of cleaning laboratory glassware. Most of the time, these methods are tried in this order:

1. A detergent solution may be used to soak glassware. This removes grease and loosens most contamination.
2. Scrubbing with a brush or scouring pad is a mechanical means of removing gross contamination and large particles. A burette or test tube brush can be used in the cleaning of burets and the neck of volumetric flasks.
3. Sonicating the glassware in a hot detergent solution is an alternative to both a detergent solution and scrubbing.
4. Solvents, such as mild acids, known to dissolve a specific contamination may be used to remove trace quantities.
5. If glassware becomes unduly clouded or dirty or contains coagulated organic matter, the following cleaning methods are recommended. They are usually used after normal cleaning has failed, and they are often used together, because each is effective at removing different types of contaminants. Care must be taken using either one because of the corrosive nature of the solutions used.
    a. If the contaminant is a metal-containing compound, soak the piece of glassware in a 6 M HCl solution. DANGER! This solution can cause severe burns! Wear appropriate gloves!
    b. If the contaminant is organic, submerge the item in a base bath (a saturated NaOH or KOH solution in ethanol or methanol). DANGER! The base bath will dissolve skin and alcohols are flammable!
6. Once the contamination has dissolved, copiously rinse the item with tap water, and then repeat the general cleaning steps above.
7. If glassware becomes greasy, it must be cleansed with chromic acid cleaning solution. The dichromate should be handled with extreme care because it is a

powerful corrosive and carcinogen. When chromic acid solution is used the item may be rinsed with the cleaning solution or it may be filled and allowed to stand. Once the contamination has dissolved, copiously rinse the item with tap water, and then repeat the general cleaning steps above.

8. Acetone may be used for a final rinse of sensitive or urgently needed glassware as the solvent is miscible with water, and helps dilute and wash away remaining water from the glassware.
9. Glassware is often dried by suspending it upside down to drip dry on racks. Glassware, other than volumetric glassware can be dried by hot (110-120) ºC-air fan to blow the internals dry. Another alternative is to place the glassware under vacuum, lower the boiling points of the remaining volatiles.

## III.4 Basic laboratory procedures

### III.4.1 Weighing

The mass describes the inertia of an object. The SI unit of the mass (*m*) is the kilogram (kg). 1 kg mass is equal to the mass of the international prototype of the kilogram kept in Sèvres on the outskirts of Paris (etalon mass). The most frequently used submultiple units of mass is the *gram* (1 g = $10^{-3}$ kg), the *centigram* (1 cg = $10^{-2}$ kg), the *milligram* (1 mg = $10^{-3}$ g) and the *microgram* (1 µg = $10^{-6}$ g).

In practice mass is determined by weighing. The laboratory equipment to determine mass is the *balance*. Early analytical balances were entirely mechanical with two weighing pans, one for the chemical, and one for the *counterweights*. The product of the mass times the distance from the balance point to the fulcrum determines the moment about the fulcrum. When these are equal for sample and standard (i.e., counterweight), the pans will be level and the balance beam horizontal.

Weighing in the laboratory is typically performed for two reasons: a.) to determine the mass of an object or a given amount of substance, or b.) to weigh out a given mass of a substance.

Characteristic properties of the balances:

1. *tolerance limit* (capacity)– the highest load, which should not be exceeded
2. *sensitivity* – the minimum amount that the balance can measure
3. *precision* – the percentage difference between the real and the weighed mass
4. *reproducibility* – the deviation of measurements at sequential weighing of the same object.

*Precision* of a balance largely depends on the condition of the *wedges*. For saving the wedges an arrester is used that supports the arms and the pans of the unused balance. In this case, the wedges are not loaded by the arms and the pans. When balancing, in an unlocked state, the arm and the pans load the wedge, and they can move freely on it.

The balance always has to be placed to a vibration-free, solid basement and has to be kept away from water vapour, acid vapour, draft and radiator. Before balancing, the level indicator on the balance has to be checked to make sure that the balance is level. Height of two legs of the balance can be changed by means of the screw thread. Changing the height of the legs the balance can be set into a perfect horizontal position.

An analytical balance is built into a glass cabinet to eliminate interfering effect of air flow. The latest types of automatic analytical balances are equipped with vibration attenuator devices and even with optical tools (lenses, mirrors, light source).

### III.4.1.1 Limit of detection of different types of balances

The type of balance used is determined by the amount of substance to be weighed and the aim of the weighing process. The most common weighing instruments in the laboratory are the *equal-arm (or beam) balances*, the *precision weighing balances*, the *analytical balances* and the *microanalytical balances*. Mechanical balances have recently been substituted by their digital counterparts.

*Equal-arm (or beam) balance*: The simplest type of balance. It is used to perform measurements with a precision is 0.01 g. The mass limit is 500 g.

*Precision weighing balance*: It can be used to perform measurements with 1 mg (0.001 g) precision. The limit of capacity is between 100–200 g.

*Analytical balance:* It is used to perform measurements with 0.0001 g (0.1 mg) precision. The limit of capacity is between 100–200 g.

*Microanalytical balance:* Very sensitive analytical instrument with $10^{-6}$ g (1 µg = $10^{-6}$ g). The weight tolerance limit is 20 g. Vibration free environment is essential for its proper (precise) operation.

*The equal-arm (or beam) balance* (Figure III.-10; a) is a simple balance in which the distances from the point of support of the balance-arm beam to the two pans at the end of the beam are equal. During measurements, the object to be weighed is placed on the left pan and the standard weights are put onto other pan until the pans are balanced.

*Analytical balances* (Figure III-10; b) are very sensitive balances. They are kept in a glass cabinet to protect them from dust and air flow. Their weighing capacities are from 100g to 200 grams. Principally, they are operating similar to the beam balances. Analytical balances have to be settled at a vibration free place; even the smallest vibration might cause a wrong result. Accordingly, analytical balances have to be placed on a specially designed *antivibration balance table* and should be stored and used in a room free from dust and acid vapour, having a constant temperature. (It is practical to use them in a separate room.)

**Figure III-10:** Laboratory balances

equal-arm (or beam) balance (a) analytical balance (b) digital balances (c)

Early *equal-arm (or beam)* (a) and *analytical balances* (b) operate on the traditional mechanic way. Nowadays balances of with such sensitivities are operating as hybrids using both mechanical and electronic technical solutions having a single pan for the substance to be weighed. In the case of these (so called *electronic*) *balances*, however, the unknown mass is also compared with definite elements of reference mass series.

The *digital balances* with different sensitivities (Figure III-10; c) operate on basis of piezoelectricity or electromagnetic compensation. These balances have built in calibration weights and they can be validated or recalibrated on the site of use. Several data storage and processing units are built into, so these balances are useful for serial measurements.

#### III.4.1.2 Rules to be followed when using analytical balance

1. The balance should be placed at a vibration free place with a constant temperature and free from corrosive fumes.
2. Never use the balance for weighing of object of higher mass then is the capacity of the balance! Information about the capacity of the balance is usually given in the front panel of the balance.
3. The balance always has to be in a horizontal position. Adjust the height of feet of the balance until the level indicator shows that the balance is level. The air bubble must be within (ideally: in the middle) of the circle on the indicator.
4. Before performing the measurement, doors of the balance cabinet should be kept open for 5-10 minutes; so that the temperature of air in the balance becomes equal to that of the environmental temperature.
5. Center the sample as precisely as possible. If the load is not in the middle of the weighing pan (off-centre or eccentric loading), the weight readout might be slightly skewed (off-centre loading error).
6. When balancing – to avoid the interfering effect of the air flow – the door of the box of the balance, always has to be kept open.
7. Allow samples to reach room temperature before weighing. Samples that are too hot will set up convection currents and the apparent sample weight will be incorrect. A slowly drifting apparent sample weight is indicative of this problem.
8. Chemicals should be placed in a weighing bottle, a plastic weighing tray, or coated weighing paper. Weighing paper is best for small quantities (usually <1g); weighing trays are used for larger amounts; and stoppered weighing bottles are recommended for reactive, volatile, toxic or hygroscopic substances. In the absence of a weighing bottle, a small beaker and watch glass may be substituted. Never place chemicals directly on the pan!
9. After finishing the measurement, the load of the balance has to be stopped in the shortest period of time. Mordant acids and alkalis must not be placed near the balance, because their fumes might attack the parts of the balance.
10. If a solid is spilled inside the weighing chamber, carefully remove it with the balance brush. The desiccant should be replaced or regenerated when it changes colour. Used weighing papers and trays should be immediately discarded. If drops of liquids spilled inside the weighing chamber, the liquid should be absorbed by a blotting paper and the contaminated area should be wiped with an alcoholic paper towel.
11. The analytical balance should be kept clean at all times. The general laboratory rules are valid in the measuring rooms. Eating, drinking and smoking are prohibited

### III.4.1.3 Experimental task: Determination of mass of objects. Weighing of solid compounds on laboratory and analytical balances.

#### III.4.1.3.1. Measurement the mass of a substance/object on a laboratory balance

- Put the object to be measured to the left pan of the balance.
- Estimate the mass of the object.
- Put the estimated quantity of reference mass units to the right pan of the balance.
- Add or take away the necessary amounts of standard mass units to set the equilibrium of the balance.

#### III.4.1.3.2. Measuring out a predetermined mass of a substance

This technique is often used to obtain a desired mass of a solid chemical, such as table salt, that exists in a granular or crystalline state. Never place chemicals directly on the pan! A piece of paper or a container of some kind, such as a watch glass, should be placed on the pan to hold the substance. The pre-set mass must be equal to the container (called the "tare") plus the mass of substance to be measured. Liquids may also be weighed in this way, using beakers or graduated cylinders.

#### III.4.1.3.3. Weighing on analytical balance

To use an analytical balance, complete the following steps.

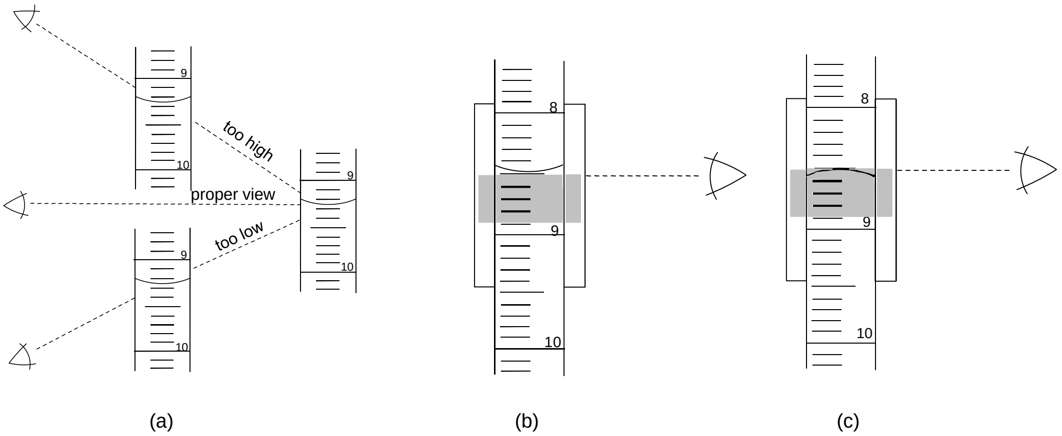
- On turning on, the display should read 0.0000 g. If it does not, press the „Zero” button or 'T' (Tare) bar beneath the display once, and wait for zero to appear. Be patient; every touch represents a command which the balance will follow.
- Since reagents cannot be weighed directly on the pan, you will first need to weigh a container. Record the first steady reading with a 'g' on the right side. Readings for light containers may fluctuate, so take the first reading with a 'g' on the right side that stays on the display for 3 seconds or longer.
- Keep the balance doors shut to prevent any draft in the lab from effecting the balance reading
- Next, add the substance whose mass you want to measure to the container. Again, record the first steady reading that stays on the display for 3 seconds or longer. The mass of the substance is the difference between the second reading and the first one.
- All objects to be weighed should be at room temperature. Objects that are either too warm or too cold will have an effect similar to a draft and result in an inaccurate reading.
- Once you're finished, gently remove the container with the substance and let the display return to zero. If it does not, press 'Tare' once. Clean immediately any spilled solid using the brush stored inside the balance. Close all open doors.

### III.4.2 Measurement of volume

The SI unit of the volume is the cubic meter ($m^2$). In practice, its $1/10^3$ part ($dm^3$) and $1/10^6$ ($cm^3$) part is also used. The litre ($1\ l = 1\ dm^3$), and $1/10^3$ part of it ($1\ ml = 1\ cm^3$); can also be used as volumetric units. The volume of gases and liquids can be determined directly, while the volume of solid object/substance can be determined indirectly, based on the volume of liquid that is displaced by the solid object/substance (*Archimedes' principle*).

Measurement of volume of liquids is a simple procedure. Reading the level of the adjusted liquid (*meniscus*), or adjustment the *meniscus* (curvature of the surface of a liquid is in a narrow tube) has to be made with great precision. To eliminate *parallax error,* the level of the liquid should be read at eye level (Figure III-11; a). The meniscus can be either *concave* or *convex,* depending on the liquid and the surface. A *concave* meniscus occurs when the particles of the liquid are more strongly attracted to the container than to each other, causing the liquid to climb the walls of the container („wetting” liquids). This occurs between water and glass (Figure III-11; b). Conversely, a *convex* meniscus occurs when the particles in the liquid have a stronger attraction to each other than to the material of the container („non-wetting” liquids). Convex menisci occur, for example, between mercury and glass in barometers and thermometers (Figure III-11; c).

**Figure III-11:** The correct reading of the levels of the fluids



When reading a depth scale on the side of an instrument filled with liquid, the meniscus must be taken into account in order to obtain an accurate measurement. Depth must be measured with the meniscus at eye level (to eliminate parallax error) and at the centre of the meniscus, i.e. the top of a convex meniscus or the bottom of a concave meniscus (Figures III-11).

Each piece of volumetric glassware is marked with its total volume, the notation TD or TC, and a temperature (usually 20 °C). The marked temperature indicates the temperature at which the apparatus was calibrated. Since density and volume change with temperature, the volume markings are strictly correct only at the calibration temperature. The notations TD and TC stand for the phrases "to deliver" and "to contain. Extensive warming (heating) of calibrated glassware is prohibited!

### III.4.2.1 Volumetric glassware

Volumetric glassware is specialized pieces of glassware which are used to measure volumes of liquids very precisely in quantitative laboratory work. Volumetric glassware can be classified if they are calibrated to contain or to deliver (Figure III-6.)

*Glassware calibrated to contain* can contain accurate volume of liquid but that pouring the liquid into another container will not necessarily deliver the indicated volume. The most important ones are the *volumetric flasks* and the *graduated cylinders*. These tools are used for preparation of solutions with known concentration.

The *volumetric flask* is calibrated to contain a fixed amount of solution with high accuracy. The flask is used in two major ways. In one technique, a sample of known mass (the solute) is placed in the flask and dissolved. The solution is then made up to the mark on the flask by adding solvent, giving a solution of precisely known volume containing a precisely known amount of solute. If the solute is pure ("primary standard" grade) or its percent purity is known, it is then possible to calculate the molarity of the solution (moles of solute per dm3 of solution). The second use of the volumetric flask is to dilute a solution in a precisely known manner. This technique involves placing an aliquot (sample of precisely known volume) of a solution of known molarity in the flask, then diluting to the mark with solvent. The new concentration may then be calculated using the volumes of the original aliquot and the new total volume.

*Glassware calibrated to deliver is used to accurately deliver or transfer the stated volume to another container*. These are the *pipettes*, (c), the *graduated measuring pipettes* (d) and the *burettes* (e). These tools are used for measurement of volume of the delivered liquids. They cannot be used to for preparation of solutions with known concentration! The reason of this is the fact that at the discharge of a wetting-liquid, a part of it adheres to the wall of the glass dish and it can cause an inaccuracy in the measurement, contrary at the volumetric flasks, the liquid flows back into the dish. The discharge of the liquids has to be made slowly – it is advisable to wait the time of the drainage, because at the wetting fluids, the layer of the liquid flows more slowly near the wall of the glass than inside.

*Volumetric pipettes* or *bulb pipette*s allow the user to measure a volume of solution extremely accurately. These pipettes have a large bulb with a long narrow portion with a *single* or *double graduation mark* as it is calibrated for a single volume. Typical volumes are 10, 25, and 50 cm$^3$. Volumetric pipettes are commonly used to make laboratory solutions from a base stock as well as prepare solutions for titration. (Figure III-6; c). The *graduated pipettes* (Figure III-6; d) are a type of pipettes consisting of a long tube with a series of 0.1 cm$^3$ graduations. These pipettes are used for the measurement of several and different volumes, with a relatively little accuracy. To fill pipettes, gumballs (Griffin or simple pipette balls) or pistons (Pi-pumps) can be used. Filling the pipettes by moth is not allowed! (Figure III-12)

**Figure III-12:** Pipetting tools

Griffin ball and simple pipette-ball

Pi-pumps

To reduce possibilities of poisoning and increase accuracy of the measurements, use *of air displacement micropipettes* is growing. Air displacement micropipettes are a type of adjustable micropipettes that can measure volumes between about 0.1 µl to 1000 µl (1 cm$^3$). These pipettes require disposable tips that come in contact with the fluid. On simple automatic pipettes manually can be set the volume to be measured, and at the measurement of various liquids, only the pipette tips are to be changed.

Besides the manual pipettes, use of electronic pipettes shows a growing tendency. Using these tools a small keyboard helps to set the required volume. Recently, there are pipettes that are programmable and applicable for the measurement of different volumes with having several pipette tips in the same time.

### III.4.2.2 Process of pipetting

- Before using the pipet to transfer solution, it should be rinsed it with the solution to be delivered. Pour the solution into a beaker. Attach the pipet to the bulb, place the tip of the pipet into the beaker and draw solution into the pipet by releasing pressure on the bulb. Once it's filled halfway, remove the bulb and quickly place your index finger on top. Turn the pipet horizontal and gently roll it to wet the inside surface. Discard the rinse solution into an appropriate waste container. After one rinsing (or two if desired), the pipet is ready for use.
- Make sure you have enough solution in your beaker and have the beaker to which you will transfer the solution handy. Attach the pipet to the bulb to draw the solution into the pipet. Avoid drawing the solution into the bulb! Draw slightly more liquid than needed so that the meniscus is above the etched mark. Remove the bulb and quickly place your index finger on top of the pipet.
- Remove the pipet from the solution, and wipe the pipet's tapered end with a clean paper towel. Then, holding the pipet in one hand and the waste container in the other let the tapered end of the pipet touch the edge of the beaker. Bring the meniscus to your eye level and release your finger slightly from the top of the pipet so the meniscus drops slowly to the etched mark. When you think the bottom of the meniscus reaches the etched mark, reassert pressure on the top of the pipet.
- While using single-marked pipettes, slowly release the liquid into a receiving vessel (a beaker or flask) until the liquid no longer flows from the pipet. After realizing the liquid, it is necessary to wait 15-20 seconds as a ’drainage time’, while keep the tip of the pipette permanently touched the edge of the beaker. The still remaining solution is to be left in pipette. Do not blow out the small amount of liquid that remains in the pipet!
- While delivering liquids using a double-marked pipette, release the liquid into the receiving vessel until the liquid level is just above the bottom etched mark. Wait 15-20 seconds as drainage time, bring the meniscus to your eye level, and release your finger slightly from the top of the pipet so the meniscus drops slowly to the etched mark.

### III.4.2.3 Use of the burette

- Always handle burets with great care. Before use make sure that the burette is clamped to the Bunsen stand perfectly in a vertical position.
- Before starting the work, check to make sure liquid will flow smoothly through the stopcock. Add some distilled water to the burette (if it is not filled with it) and then open the stopcock and check the flow. If the liquid flows slowly or if the tip is clogged, ask for another burette. Also check for any leaks from the stopcock barrel. If there is one, try adjusting the lock nut on the side of the Teflon stopcock. If this does not stop the leak, replace the burette.
- Rinse the burette with the solution the burette will contain. Transfer some solution to a beaker and then pour about 10-15 $cm^3$ into the burette, like it was done with the deionized water. Close off the top of the burette with your finger and then turn the burette horizontally. Roll and tilt the burette so the solution wets the entire inside surface. Drain the solution into the waste container (beaker). Since we are rinsing with a solution, you should wear gloves to protect your skin.
- Fill the burette with solution above the 0.00 mark and adjust the initial level to the zero mark by firm opening of the stopcock. Notice an air gap at the bottom of the burette. The quick way to get rid of the air gap is to open and close the stopcock quickly, forcing most of the air out.

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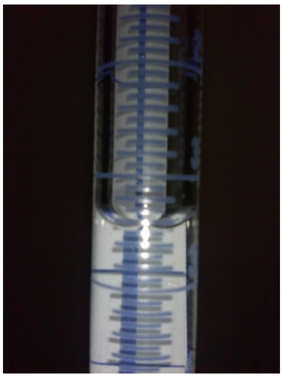
- Open the stopcock partially to control the flow of the solution. Once the desired volume is transferred from the burette – similar to the practice with pipettes – leave some time for drainage of the solution. After a while read the liquid level again. If the burette is used for titration, when approaching end of the process the solution has to be transferred dropwise to ensure correct determination of the volume delivered from the burette.
- Shellback-type burettes are designed with a blue line on a broader white band running vertically behind the scale to create an optical effect which makes the meniscus and line appear to form a point. While using a Shellback-type burette read meniscus at the narrowest point of the blue line for best results (Figure III-13).
- When you have finished the work, empty the burette into a waste container and rinse it well with deionized water.

**Figure III-13:** Shellback-type burette



### III.4.2.4 Calibration of a volumetric flask and a pipette

### III.4.2.4.1. **Calibration of a volumetric flask**

Pipette calibration is an important consideration in laboratories. It is the act of examining or adjusting the quality of being near to the true value of a measuring device by comparison with a standard.

The calibration process is usually performed by weighing the amount of water contained in the volumetric flask. Before calibration the flask should be cleaned carefully (degreasing, rinsing with acetone) and dried without warming. The mass of the empty flask ($m_e$) is measured by an analytical balance. Then the mass of the flask properly filled to the mark with distilled water of known temperature is established ($m_{e+d}$). It should be ensured that the flask is completely dried outside. The result of the calibration has to be determined by three parallel measurements.

Using of the following formula the results of the measurements give the real volume of the flask:

$$V_{corr} = \frac{m_{e+d} - m_e}{\rho_d}$$

where:

$\rho_d$ = density of distilled water at the temperature of measurement (g/cm$^3$)
$m_{e+d}$ = mass of the flask filled with distilled water (g),
$m_e$ = mass of the empty flask
$V_{\mathrm{corr}}$ = corrected, actual volume of the flask (cm$^3$)

### III.4.2.4.2. **Calibration of a pipette**

A glass-stoppered, empty, properly cleaned beaker ($m_e$) is weighed by an analytical balance. The pipette to be calibrated is filled with distilled water of known temperature. The nominal volume of the pipette is transferred into the beaker as described above (see III.4.2.2.) Than, mass of the flask containing the distilled water, is measured again ($m_{e+d}$). The result of the calibration has to be determined by three parallel measurements.

Based on the difference of the two measurements ($m_{e+d} – m_e$) the mass and the corrected volume ($V_{corr}$) of the delivered amount of distilled water can be calculated. Calculation of the corrected volume should be performed using the above formula used for calibration of volumetric flasks.

## III.4.3 Measurement of density

Density ($\rho$) is the mass ($m$) of the volume ($V$) unit of a substance:

$$\rho = \frac{m}{V}$$

$$\rho = \frac{m}{V} \rightarrow m = \rho \cdot V$$

The SI unit of the density is the $kg \cdot m^{-3}$. In practice, both $g \cdot cm^{-3}$ and $g \cdot dm^{-3}$ units are also used.

The density of a material varies with temperature and pressure. This variation is typically small for solids and liquids but much greater for gases. Increasing the pressure on an object decreases the volume of it and thus increases its density. Increasing the temperature of a substance (with a few exceptions) decreases its density by increasing its volume.

The density of a compound determined at 0 °C is called *normal density*. Density of the same compound at a $t$ temperature ($\rho_t$) can be calculated from the change in the volume. Densities and volumes measured at different temperatures are inversely proportional to each other.

$$\rho_t : \rho_0 = V_0 : V_t$$

So:

$$\rho_t = \frac{\rho_0 \cdot V_0}{V_t} = \frac{\rho_0 \cdot V_0}{V_0(1+\alpha t)}$$

where $\alpha$ is the *cubic heat expansion coefficient*.

The density determined above is called *absolute density*. To simplify comparisons of density across different systems of units, it is sometimes replaced by the dimensionless quantity *relative density*, i.e. the ratio of the density of the material to that of a reference material. The reference material for gases is usually dry air, while for liquids and solids are water. The *relative density* is the ratio of two absolute densities that are in the same physical conditions (same pressure and temperature).

If the reference material is not explicitly stated then it is normally assumed to be water at 4 °C (or, more precisely, 3.98 °C, which is the temperature at which water reaches its maximum density). Thus, the *relative density* of solids or liquids is the ratio of mass of unit volume of the tested material measured at 20 °C to the mass of unit volume of water measured at 4 °C. The symbol for relative density is $d^{20}_{4}$. The (absolute) density of the water on 4 (3.98) °C is approximately 1000.00 (999.9720) kg/m$^3$ = 1.00000 (0.999972) g/cm$^3$, which makes relative density calculations particularly convenient: the density of the object only needs to be divided by 1000 or 1, depending on the units.

Relative density can be calculated directly by measuring the density of a sample and dividing it by the (known) density of the reference substance. In practice, density of liquids is determined most frequently. For determination of densities of liquids *hydrometer*, *pycnometer*, *hydrostatic balance* (*Mohr-Westphal* balance) and *digital densitometers* can be used.

The density of liquids can be conveniently and quickly determined by hydrometers. This consists of a bulb attached to a stalk of constant cross-sectional area (Figure III-14; a).

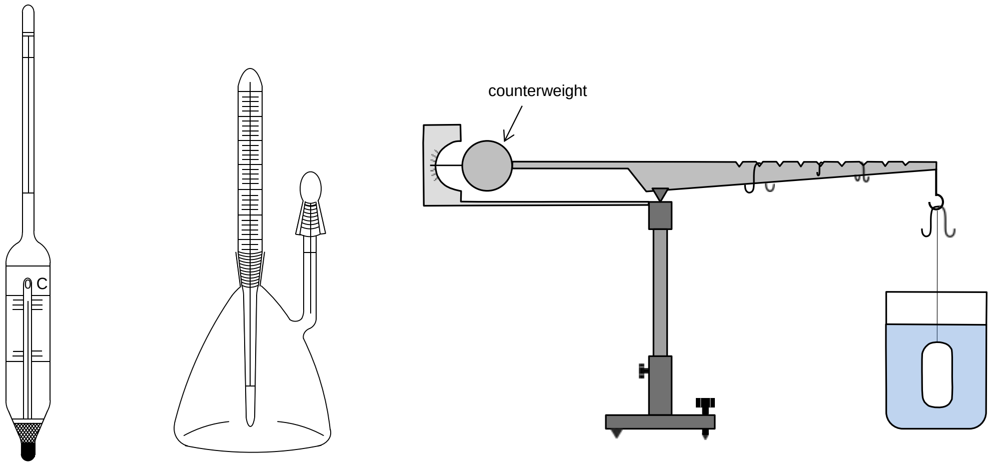
First the hydrometer is floated in the reference liquid and the displacement (the level of the liquid on the stalk) is marked. The reference could be any liquid, but in practice it is usually water. The hydrometer immerses into the liquid until the weight of the discharged liquid is equal with the weight of the hydrometer (*Archimedes's principle*).

The hydrometer is then floated in a liquid of unknown density. The change in displacement is noted. Application of simple physical principles allows the relative density of the unknown liquid to be calculated from the change in displacement.

It is, of course, necessary that the hydrometer floats in both liquids. A hydrometer can be applied only in a definite range of density. Accordingly, two types of hydrometers are used. "*Search hydrometers*" are applied for determination of the approximate density of the tested liquid to find the appropriate measuring range. For accurate measurements "*measuring hydrometers*" can be used, which are operating in the relevant (narrow) density range.

A *pycnometer* is a device used to determine the density of a liquid. Using pycnometers, measurement of density is based on measurement of mass and volume: mass of liquid of known volume is measured and the density is calculated from the measured data. A pycnometer is a bottle with a capacity of usually 10 cm$^3$ to 100 cm$^3$, having a ground-glass stopper fitted with a thermometer, and a side inlet-tube with a marked line and a close-fitting ground glass stopper (Figure III-14; b). This device enables a liquid's density to be measured accurately by reference to an appropriate working fluid, such as water, using an analytical balance.

**Figure III-14:** Tools for density measurement.



(a) (b) (c)

Since density is function of temperature, it is necessary to measure the temperature of the sample. After setting the meniscus into the proper position, the side a side inlet-tube can be closed with a glass stopper and practically there is no evaporation loss. If the flask is weighed empty, full of water, and full of a liquid whose relative density is desired, the relative density of the liquid can easily be calculated. The mass of the empty pycnometer is subtracted from masses of the filled pycnometer, and because their volumes are the same, their ratio of density is the same as their ratio of masses.

Density measurement of liquids by hydrostatic method is based on *Archimedes' principle*. Determination is based on measurement of mass reduction of a reference glass body (plummet) of known volume in liquids with known and unknown densities. These measurements can be performed using a *hydrostatic* or a *Mohr-Westhphal balance*.

The *Mohr-Westphal balance* (Figure III-14; c) is an unequal-arm balance designed for determining the density of liquids and solids by hydrostatic weighing. The heaviest unit of the counterweight series - a U shaped nickel-plated brass wires - has a weight equal to the reduced weight (to vacuum) of that volume of water of 4 °C which is equal to the volume of the plummet. The smaller counterweights (called *riders*) are the 0.1, 0.01 and 0.001 parts of weight of the main unit. If the weight loss of the plummet is measured by these series of counterweights, the density will be given directly as the weight loss of the plummet.

To operate a Mohr-Westphal balance care must be taken to first calibrate the balance by means of the levelling screw at the bottom of the body. With no weight on the arm of the balance the two pointers must be aligned before the balance can be used. Then the plummet is fully immersed into distilled water of 4 °C temperature. To reset the equilibrium position of the balance the heaviest counterweight have to hang on the No 10 position (tenth notch) of the bar; because the density of distilled water at 4 °C is 1.0000 g/cm$^3$. If the plummet is immersed into a liquid of density of 1.354 g/cm$^3$, one of the two largest weight units has to be placed to the end (first notch) of the bar, while the 0.1 unit counterweight is to be placed onto the third notch, and continuously, the 0.01 unit counterweight onto the fifth and the 0.001 unit counterweight have to be placed onto the fourth notch of the arm to balance the scale.

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With the use of the Mohr-Westphal balance, the density can be determined conveniently with three-decimal-precision without performing calculations, but this method does not reach the accuracy of measurements with a pycnometer.

### III.4.3.1 Experimental task: Determination of density of sodium chloride and ammonium chloride solutions of unknown concentrations

#### III.4.3.1.1. **Measurement with pycnometer**

The mass of the dry pycnometer (with its stopper) has to be weight accurately by an analytical balance. The pycnometer should be filled entirely with the liquid of which density is to be determined. When closing the pycnometer, a special attention has to pay that there should not remain any air bubbles in the liquid and the any spilled fluid has to be wiped off from the outer side of the glassware. The measurement can be achieved by three consecutive weighing. First, the mass of the clean and dry pycnometer has to be measured by an analytical balance ($m_1$), then, after taking off the stopper and the capillary of the pycnometer, it is to be filled with distilled water at room temperature. The capillary and the stopper have to be replaced to the dried measuring dish and perform the weighing repeatedly ($m_2$). The volume of the dish ($V$):

$$V = \frac{m_2 - m_1}{\rho_{water}}$$

$\rho_w$ is the density of the used distilled water (with four decimal precision) at the temperature of the measurement.

After the measurement, the water is discarded; the pycnometer is rinsed with the test liquid. Then, similar to the measurement with distilled water, the dish is filled with the test liquid. The properly filled dish is weighed again ($m_3$). The mass of the liquid in the dish:

$$m_t = m_3 - m_1$$

Based on the mass of the liquid ($m_t$) and the volume of the pycnometer the density of the liquid can be calculated:

$$\rho_t = \frac{m_t}{V} = \frac{m_3 - m_1}{V} = \frac{m_3 - m_1}{m_2 - m_1} \cdot \rho_{water}$$

#### III.4.3.1.2. **Measurement with Mohr-Westphal balance**

To operate a Mohr-Westphal balance care must be taken to first calibrate the balance by means of the levelling screw at the bottom of the body. With no weight on the arm of the balance the two pointers must be aligned before the balance can be used. Then the plummet is fully immersed into distilled water of 4 °C temperature. To reset the equilibrium position of the balance the heaviest counterweight have to hang on the No 10 position (tenth notch) of the bar; because the density of distilled water at 4 °C is 1.0000 g/cm$^3$. This will be the equilibrium state of the balance and this density is to be compared to that of the test solutions. The exact temperature of the distilled water sample is noted.

After the first measurement the distilled water is discarded, the plummet is wiped dry and rinsed with the test solution. The measuring cylinder is filled with the test solution and then measurement of density of the test solution can be performed. During the measurement the counterweight units have to be placed on the arm in an order of their decreasing weights. As a first attempt, the two pointers are tried to be aligned by the largest weight. If it is unsuccessful, than place the smaller weights in decreasing order onto the notches of the arm. The trials are continued until two pointers are aligned as it was the case with distilled water. To determinate the relative density of the solution, positions of the counterweights in decreasing order is to be read.

Finally, the real density of the solutions is to be calculated from the measured relative density.

### III.4.4 Measurement of temperature

Temperature is the numerical measure of the thermal state of a body. The device for measurement of temperature is the *thermometer*. For measurement of temperature any material property can be used that show a regular correlation with the temperature, by other words, changing the temperature results in a well detectable, regular and reproducible change in the numerical value of the material property. Such properties are the *thermal expansion*, the *electric conductivity*, *light phenomenon*, *thermoelectric force between metals*, etc.

A thermometer operates accurately if its temperature equal to the temperature of its surroundings. The thermal equalization needs a certain period of time. Therefore, the reading the temperature has to be made in equal intervals (e.g. in every 0.5-minute-time) until the same results are obtained in 3-5 consecutive timepoints.

To avoid the parallax error the thermometer is to be read in a perpendicular position to the mercury column. Because of the thick wall of the glass capillary, in case of *long-stem thermometers* the chance of the parallaxes error can be particularly high.

In the SI system, the thermodynamic temperature (T) is the basic thermal measure. The unit of thermodynamic temperature is *kelvin* (K). The *kelvin* is the 1/273.16 fraction of the thermodynamic temperature of the triple point of water. The Celsius degree of temperature is a derived unit of the thermodynamic temperature. The symbol of temperature expressed in Celsius degrees is $t$, and the symbol of the unit °C. 1 °C is 1/100 part of the thermodynamic temperature difference of the temperature of the melting point and boiling point of water. 1 K temperature difference is equal to 1 °C temperature difference. The relation between the two temperature scales is: $t = T - 273.15$.

Measurement of temperature is generally carried out by *liquid-in-glass thermometers*. A liquid-in-glass thermometer consists of a narrow, sealed glass tube with a bulb filled with mercury, alcohol (usually dyed red, to make it easily visible), or some other liquid at its lower end. As the temperature rises, the liquid expands and rises in the tube. A drop in temperature causes the liquid to contract, so that its level in the tube falls.

Liquid-in-glass thermometers are generally made of glass and mercury, amyl alcohol or isopentane used as filling liquids. In the – 10 °C to + 200 °C temperature range it is the mercury-in-glass thermometers that are the most frequently used. When measuring lower temperatures e.g. until -100 °C, amyl alcohol and until -200 °C isopentane are used as filling liquids. As of 2012, many mercury-in-glass thermometers are used in meteorology; however, they are becoming increasingly rare for other uses, as many countries banned them for medical use due to the toxicity of mercury.

A *long stem thermometer* is a thick walled capillary tube, at which the scale is etched onto its outer surface. In a thermometer with an inner scale a thin walled inner capillary tube filled with a liquid is placed in front of a milk glass plate, onto which the scale is engraved. These thermometers generally cannot be used for measurements with higher than 0.1 °C precision.

In a small temperature interval (5-6 °C), *Beckmann thermometers* can be used to perform measurements with a higher precision (0.01 °C). These thermometers can be used at any temperature range, because the mercury content of their bottom bulb can be altered with the help of a reserve vessel on the top of these thermometers.

Besides the liquid thermometers, further kind of thermometers to be mentioned are those based on: a.) thermic expansion of metals (called: *bimetallic thermometers*); b.) change of pressure of a gas (called: *manometric (or gas) thermometer*), c.) change of resistance of metals (called: *resistance thermometers*), and d.) difference in conductivity (called: *thermoelectric thermometers*) can be mentioned. The usage of these latter mentioned thermometer types in the chemical laboratory is rare.

### III.4.5 Warming and boiling

Laboratory instruments can be warmed with direct or indirect heating equipment. The *Bunsen burner*, the *electric hot plate***,** or the *electric heating mantels* operate by direct heat transfer. Frequently, especially when working with flammable compounds, warming should be performed using heat-transfer mediators (e.g. heating baths). As a heat-transfer mediator, water, oil and sand is used in most of the cases.

Solid compounds are heated in crucibles. Generally, crucibles are made of porcelain; they are placed into a *clay triangle* put onto a *Bunsen-tripod* and heated with direct flame from a *Bunsen burner*.

When large number of samples has to be ignited or high temperature should be applied, automatically controlled *electric ovens* can be used.

Small volumes of aqueous solutions can be warmed in test tubes heated with direct flame from a *Bunsen burner*. Direct heating of test tubes should be done cautiously with mild shaking. Care has to be taken that the volume of liquid in the test tube (with a volume of 20 $cm^3$) should not be more than 4-5 $cm^3$, even after mixing of all the reactants. When boiling, the test tube can be held with the use of a *test tube clamp*. *The mouth of the tube is never to be pointed at ourselves or anyone else.*

A larger amount of non-flammable and not too volatile liquid can be boiled in an *Erlenmeyer flask* or a *beaker* is placing the glassware onto an *asbestos wire gauze* (heated by a *Bunsen burner*) on a an *electric hot plate*. In order to avoid overheating or foaming, a few pieces of boiling stone should be put into the liquid. Heating always has to be started with a small flame.

Small quantities of flammable liquids can be heated under the hood on an electric *hot plate* or in an *electric water bath*. A larger quantity of such liquids can be heated in a ground glass flask equipped with a reflux condenser in an *electric water bath* or in an *electric heating mantle*.

### III.4.6 Melting point determination

The *melting point* of a solid is defined as the temperature at which the solid and the liquid phases are in equilibrium at a total pressure of 760 Hgmm (101,325 kPa). The melting point is a physical property fundamentally depended on the structure of a compound. The melting point can be determined with high accuracy because the temperature of pure crystalline solids remains constant until the solid phase is present. During the melting process the amount of the convected heat provides the *heat of fusion*. While melting, the temperature of the melting solid remains constant; the transferred amount of heat is used to provide the *heat of fusion* needed for the solid–liquid transformation. Pure crystalline substances have a sharp melting point can that be observed within 1 °C range.

The factors that affect the melting point of a substance are: a.) the degree of purity; b.) the amount and nature of impurity; and c.) crystallization water and moisture content.

Factors affecting the accuracy of melting point determinations are: a.) the amount of available substance; b.) the equipment used for determination; and c.) the rate of heating.

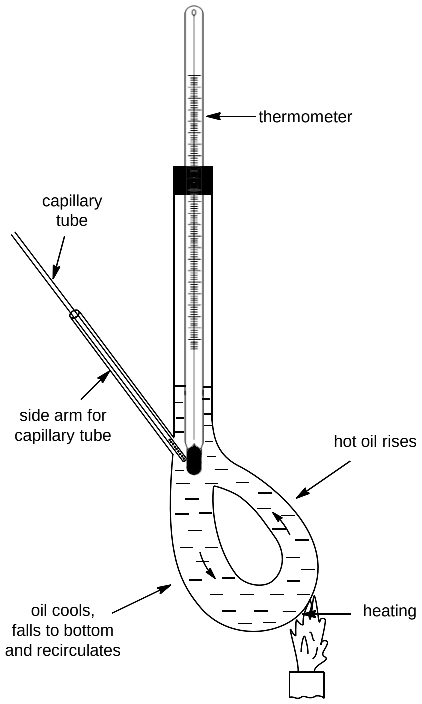
Soluble impurities in the molten substance reduce its melting point. Furthermore, a contaminated substance generally does not melt at a fixed temperature, but the melting process take place over a certain temperature range. The so called *eutectic mixtures* behave different way; they have a sharp melting point like pure compounds: they have a definite, permanent melting point that belongs to the eutectic composition.

There are compounds that undergo decomposition around their melting point. In such cases, the melting process is prolonged; before melting, the compound gets discoloured, turns brown and gases might be evolved. Such substances have *decomposition range*.

There are several methods by which melting points can be determined, and the choice of method depends mainly upon how much material is available. An approximate melting point can be determined in a relatively short time by the apparatus shown on the Figure III-15. The main body of the apparatus loop-shaped glassware (*Thiele tube*) which is filled up with silicone oil. A thermometer is fitted to the top of the glassware and a capillary tube closed at one end, containing the sample, can be placed through sidetubes. The bottom part of the thermometer and that of the capillary is immersed into the silicon oil.

Once the setup has been complete, the lower part of the side arm of the Thiele tube is carefully heated with a small flame from the *Bunsen burner* moving the flame back and forth along the arm. The shape of the *Thiele tube* allows for formation of convection currents in the oil when it is heated. The thermometer and sample must be at the same temperature while the sample melts, so the rate of heating must be slow as the melting point is approached (about 1 $^{o}$C/min). Otherwise, the temperature of the thermometer bulb and the temperature of the crystals in the capillary may not be the same. The transfer of heat energy by conduction takes place rather slowly.

**Figure III-15:** Equipment for melting point determination (Thiele tube**)**



A quick and easy method to determine the melting point of a solid is to heat the capillary tubes containing the sample in an electrically heated metal block, while observing the crystals with the aid of a magnifying glass. This method requires as little as a few crystals and it is very convenient.

**Figure III-16:** Electrically heated melting point measurement devices.

Melting point of a very small amount of a substance (as little as few crystals) can be made by the *Kohler's microscope with a heatable stage* (Figure III-17). The most important parts of the device are a heatable metal block and a microscope. The temperature of the meal block can be finely controlled and heated up to 350°C. In the middle of the block table there is an opening of 1.5 mm in diameter for transmission of light. A few crystals of the sample between a pair of microscope cover glasses are placed on the electrically heated metal block while observing the crystals with the aid of the microscope. Graduation of a thermometer – showing the actual temperature of the heating block - can also be displayed on the field of vision of the microscope, so the temperature and melting of the compound can be simultaneously observed.

**Figure III-17:** Kohler's microscope with a heatable stage.

### III.4.6.1 **Experimental task:** Melting point determination of a known (urea) and an unknown compound

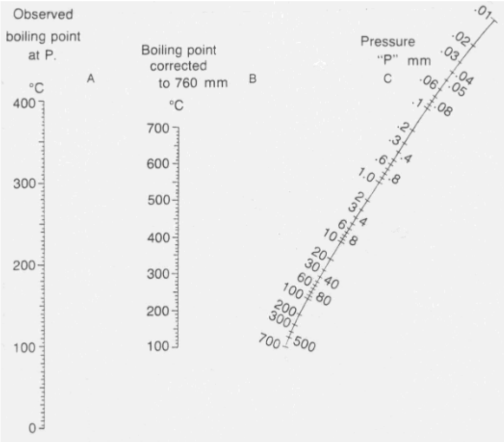
1. **Training measurement with urea**
   a. The urea sample, if it is necessary, is pulverized in a mortar and a capillary tube carefully sealed on one end is filled with it. Usually, the melting point capillary can be filled by pressing the open end into a small heap of the crystals of the substance, turning the capillary open end up, and vibrating it by drawing a file across the side to rattle the crystals down into the bottom. If filing does not work, drop the tube, open end up, down a length of glass tubing about 1 cm in diameter (or a long condenser) onto a hard surface such as a porcelain sink, stone desk top, or a watch glass. It is practical to fill the capillary in a 1–1.5 cm length; the sudden contraction of the compound indicates clearly the formation of the new phase.
   b. Immerse the capillary into the *Thiele* tube that the test sample has to be exactly in front of the mercury bulb of the thermometer. Thus, the temperature close to the capillary and the mercury bulb of the thermometer is very much the same.
   c. The thermometer and sample must be at the same temperature while the sample melts, so the rate of heating must be slow as the melting point is approached (about 3-5 $^{o}$C/min). Otherwise, the temperature of the thermometer bulb and the temperature of the crystals in the capillary may not be the same.
   d. Warm the lower part of the side arm of the Thiele tube carefully with a small flame from the Bunsen burner moving the flame back and forth along the arm. At the first preliminary measurement warm the apparatus allowing the temperature to rise at a rate of 10 °C/min.
   e. Note the temperature when the edges of the crystals start to melt. The temperature range over which the sample is observed to melt is taken as the melting point.
   f. Remove the capillary containing the molten compound and allow the apparatus to cool 30°C below of the measured melting point.
   g. After the preliminary measurement at least two more accurate determination, with a low rate of heating (about 3–4 °C/min) near the melting point. Provided that the average of the two latter measurements is close to 133 °C, the melting point of urea, melting point determination of the unknown compound can be started.

2. **Melting point determination of an unknown substance**
   a. The unknown compound, if it is necessary, can be pulverised in a mortar, then similar to the previous determination, the compound is filled into a capillary carefully sealed on one end. If it possible, larger crystals should be used, because the melting edges of the crystals can be observed better on these.
   b. The capillary is placed into the melting point measuring apparatus that the sample should be in front of the mercury bulb (see above).
   c. Warm the apparatus with a Bunsen light at a rate of 10 °C/min, and note the temperature when edges of the crystals start to melt. The temperature range over which the sample is observed to melt is taken as the melting point.
   d. Remove the capillary containing the molten compound and allow the apparatus to cool 30°C below of the measured melting point.
   e. After the preliminary measurement at least two more accurate determination, with a low rate of heating (about 3–4 °C/min) near the melting point

### III.4.7 Boiling point determination

If a sample of a liquid is placed in an otherwise empty space, some of it will vaporize, and the pressure in the space above the liquid will rise to some constant value. The pressure under these conditions is due entirely to the vapour of the liquid, and is called the equilibrium vapour pressure. The vapour pressure depends on the temperature: the higher the temperature the higher the equilibrium vapour pressure. The temperature at which the equilibrium vapour pressure equals the pressure of the pressure above the liquid (outer pressure) is the boiling temperature. The boiling point of liquids – if there are no other specific criteria – is the temperature, at which the vapour pressure equals the see-level atmospheric (101,325 kPa) pressure. To get the boiling point, the determined boiling temperature has to be converted to 760 Hgmm (101,325 kPa), by means of a simple tool, called nomograph (Fig. III-18). Application of this chart is rather useful, since vapour pressure shows not an easily computable linear, but an exponential temperature dependence (*Clausius-Clapeyron* equation).

**Figure III-18:** Pressure-temperature nomograph

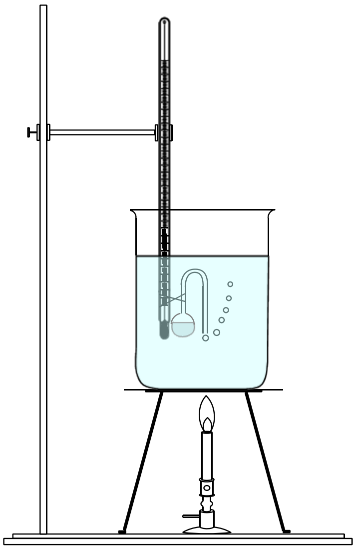


While boiling – if the outer pressure is constant - the temperature of the boiling liquid remains constant; the transferred amount of heat is used to provide the heat of evaporation needed for the liquid–vapour transformation. The boiling point of a substance available in a large quantity can be determined by distillation (Chapter III-

5.4.). Care must be taken during distillation that boiling should be consistent, and the thermometer should be surrounded by sufficient quantity of equilibrium vapour.

When only a small amount of liquid material is available determination of boiling point, in some cases the *Smith-Menzies* method can be applied (Figure III-19). This semi-micro method can be used for measurement of the boiling point of 0.1 – 1 $cm^3$ volume of liquid samples. However, application of the method is limited; it cannot be used (or only with a limited accuracy) if the test compound is miscible with the liquid in the heating bath (most frequently water).

**Figure III-19:** Determination of the boiling point with the *Smith-Menzies* method



When liquid mixtures are heated, the temperature of the vapour is not constant but - if the sample mixture is not azeotropic - continuously increasing over the time of boiling. Separation of components of non-azeotropic mixtures can be performed by distillation (Chapter III.5.4).

### III.4.7.1. **Experimental task**: Determination of the boiling point of an unknown liquid with a semi-micro (*Smith-Menzies*) method

The determination can be performed with the micro boiling point apparatus shown on Figure III-19.

The thin-walled sphere with a bended stem is to be filled half with the help of an eye-dropper (or with intermittently heating/cooling) with the test solution. The stem of the sphere is fixed to a thermometer with a rubber band, so that the lower end of the stem is in level with the mercury reservoir of the thermometer. Fix the thermometer to a stand and immerse it together with the sphere in water. Care must be taken that the apparatus is thoroughly immersed in the water bath (the unknown should not react with or dissolve too fast in the temperating liquid). Begin heating the bath while stirring (the rate of elevation of the temperature should be at about 1 °C in a minute). During the heating phase bubbles begin to escape from the mouth of the stem, first at a slow rate (caused by the extension of the air and liquid in the sphere). When boiling begins the rate of bubbling speeds up. Stop heating and continue stirring until the bath cools down to the temperature of the boiling point of the unknown, indicated by the last bubble stopping at the mouth of the stem. This value is the boiling temperature at pressure p, which is the pressure inside the sphere. Pressure p is higher than the atmospheric pressure with the hydrostatic pressure of the liquid column consistent with the h length of the stem of the apparatus. In order to be able to repeat the measurement without cleaning/filling the sphere again start the heating immediately, before water is sucked back into the sphere. The boiling point of the unknown should be determined at least three times separately, accepting the average of the values as a result.

### III.4.8 Dissolution

Dissolution is a process by which a solute forms a solution in a solvent. The maximum quantity of the dissolved compound depends on the nature of the solvent and the solute, the temperature and the pressure, in the case of gases.

When a solid is to be dissolved, it should be pulverized in a mortar to increase the contact surface of it. Dissolution can also be accelerated by heating and stirring. Stirring of liquids can be made by tools made of glass or metal. If homogenization needs relatively long time, the stirrer can be electrically operated. A frequently used device is the magnetic stirrer. A *magnetic stirrer* is a laboratory device that employs a rotating magnetic field to cause a stir bar immersed in a liquid to spin very quickly, thus stirring it. The *stir bar* is a small iron bar covered by glass or plastic. This procedure ensures effective homogenization of the solution.

Concentration of solutions provides information on the quantitative relation of solute and solvent. Definition of the most frequently used concentrations is discussed in Chapter V.) Depending on the quantity of solute and solvent, the solution can be *unsaturated*, *saturated* or *supersaturated*.

*Solubility* is the property of a substance to dissolve in a solvent to form a homogeneous solution. It is numerically characterized by the amount of solute (g) dissolved in 100 g of solvent. Solubility is the concentration of the *saturated solution*. A saturated solution is one in which the dissolved solute is in equilibrium with the non-dissolved solute; adding more solute does not increase the concentration of the solution. Solubility of a substance fundamentally depends on the physical and chemical properties of the substance and solvent as well as on the temperature, pressure (in the case of dissolution of gases in liquids) and the pH of the solution.

Solutions with definite concentrations can be prepared in two ways:

1. Preparation of a solution from a solid substance. When a solid substance is available, the required amount of substance is weighed out on a balance and transferred into a volumetric flask. When the compound is dissolved, the flask is filled with the solvent.
2. Preparation of a solution from a “stock solution”. This way a diluted solution is prepared from a more concentrated solution of known concentration (“stock solution”).

### III.4.8.1 Calculation examples for making of solutions

1. What volume ($cm^3$) of 96.0 m/m% concentrated sulphuric acid ($\rho = 1.86$ g/$cm^3$) is needed to prepare 0.40 $dm^3$ of 10.0 m/m% ($\rho = 1.09$ g/$cm^3$) sulphuric acid solution?

Mass of the 0.40 $dm^3$ ($\rho = 1.09$ g/$cm^3$) sulphuric acid solution:

$m = V \cdot \rho = 400.0\ cm^3\ 1.09\ g/cm^3 = 436.0\ g$

Mass of sulphuric acid in the solution:

| | |
|---|---|
| 100.0 g solution | 10.0 g sulphuric acid |
| 436.0 g | x g sulphuric acid |

x = 43.6 g

Mass of containing 43.6 g of sulphuric acid:

| | |
|---|---|
| in 100 g solution there is | 96.0 g solute |
| in *y* g | 43.6 g |

y = 45.42 g

Volume of the 45.42 g concentrated sulphuric acid:

$$V = \frac{m}{\rho} = \frac{45.42}{1.86} = 24.42\ cm^3$$

*Thus, 24.42 $cm^3$ of 96 m/m% concentrated sulphuric acid is needed.*

2. 54.0 g of 14.0 m/m% and 96.0 g of 6.0 m/m% sodium chloride solutions are mixed. Calculate the m/m% concentration of the obtained solution.

These types of problems can be calculated by the mixing equation, considering that mass is an additive property:

$$m_1 \cdot (m/m\%)_1 + m_2 \cdot (m/m\%)_2 = (m_1 + m_2) \cdot (m/m\%)_3$$

$$54.0\ g\quad 14.0\ \% + 96.0\ g \cdot 6.0\ \% = (54.0\ g + 96.0\ g)\ (m/m\%)_3$$

$$8{,}88\ \% = (m/m\%)_3$$

*Thus, concentration of the diluted sodium chloride solution is 8.9 m/m%.*

## III.4.8.2 Experimental task: Preparation of solutions of different concentrations

### **III.4.8.2.1.** Preparation of solution from a solid substance

Prepare a solution of given volume and concentration from the substance provided by the instructor. There are five major steps in preparation of the solution:

- Calculate the required amount of substance. Pulverize the compound in a mortar, then measure the required quantity into a suitable dish (beaker, weighing dish (for hygroscopic substances), etc.). Depending on the required accuracy, laboratory or analytical balance should be used.
- With continuous stirring dissolve the substance in a quantity of water that is much less than the volume of the dish. In the case of slowly dissolving compounds it is practical to gently warm up the solution.
- The total amount of the solution (cooled back, if it is needed) is transferred into a volumetric flask by means of a long stemmed analytical funnel. Rinse the beaker with small portions of the solvent several times and collect the solvent portions in the volumetric flask by means of a long stemmed analytical funnel used before.
- Fill the volumetric flask with the solvent up to the neck of the flask. Meanwhile, homogenize the content by careful shaking. After homogenization, carefully fill the flask to the mark. Move your eye to the level of the mark on the neck of the flask and line it up so that the circle around the neck looks like a line, not an ellipse. Then add distilled water a drop at a time until the bottom of the meniscus lines up exactly with the mark on the neck of the flask. Take care that no drops of liquid are in the neck of the flask above the mark.
- After closing the measuring flask, homogenize the solution.

### **III.4.8.2.2.** Preparation of solution from a ’stock-solution’

Prepare a solution of a given volume and concentration from the solution (of known density and m/m%) provided by the instructor. There are five major steps in preparation of the solution:

- Calculate how much stock solution you need. Measurement of volume of liquids is simpler then measuring their mass. With knowledge of density, calculate what a volume is needed from the stock-solution.
- Pour a small portion of distilled water into the volumetric flask through a long stemmed analytical funnel.
- The previously calculated volume of the stock solution has to be measured with appropriate volumetric glassware (generally with a pipette or - in case of serial sampling - with a burette) and transfer the total amount of the solution into a volumetric flask by means of a long stemmed analytical funnel. Rinse the funnel with small portions of the solvent several times and collect the solvent portions in the volumetric flask.
- Fill the volumetric flask with the solvent up to the neck of the flask. Meanwhile, homogenize the content by careful shaking. After homogenization, very carefully fill the flask to the mark. Move your eye to the level of the mark on the neck of the flask and line it up so that the circle around the neck looks like a line, not an ellipse. Then add distilled water a drop at a time until the bottom of the meniscus lines up exactly

with the mark on the neck of the flask. Take care that no drops of liquid are in the neck of the flask above the mark.
- After closing the measuring flask, homogenize the solution.

## III.4.9 Formation of precipitates

The opposite process of dissolution is precipitate formation. In this process, the solubility of a dissolved compound is reduced in order to separate it from other soluble components of the solution (e.g. contaminations of the dissolved compound). It can be accomplished by changing the solvent, changing the pH or the temperature of the solution, or performing a reaction in which the compound to be separated forms a product of much lower solubility. A precipitate forming process should be selected which results in formation of well filterable, coarse-grained precipitate that can be easily separated from the liquid phase. That way, contamination of forming precipitate is also prevented.

Barium chloride ($BaCl_2$) is a well soluble compound in water, but solubility of barium sulphate ($BaSO_4$) is extremely low. If barium ions should be precipitated out of an aqueous solution they should be transformed to their low solubility sulphate salt. Barium chloride reacts with ammonium sulphate to form barium sulphate precipitate:

$$BaCl_2 + (NH_4)_2SO_4 = \underline{BaSO_4} + 2\ NH_4Cl$$

To achieve quantitative conversion of barium ions into their sulphate salt, the pH of the solution should be set at pH = 2 by means of hydrochloric acid solution.

### III.4.9.1 Experimental task

#### **III.4.9.1.1.** Preparation of $BaSO_4$ precipitate

5 $cm^3$ of 5 % barium chloride solution is pipetted into a beaker, acidified with 1 $cm^3$ 1 M hydrochloric acid and its volume is completed to 100 $cm^3$ with distilled water. While boiling, 10 $cm^3$ of 2.5 m/V% ammonium sulphate solution is added dropwise, with continuous stirring of the solution. After cooling, the separated precipitate is filtered and rinsed with 5 $cm^3$ portions of distilled water several times.

# III.5 Basic laboratory separation techniques

## III.5.1 Filtration, decantation, sedimentation

The separation of the solid phase (precipitate) from the liquid phase can be managed by *filtration*, *decantation*, and *sedimentation*. The *filtration* is a mechanical operation process during which the solid particles are mechanically separated from the liquid phase. During *decantation*, the liquid is gently removed from the top of precipitate, shaken with pure washing fluid, allowed to settle, and the washing fluid is removed again. If the procedure is repeated several times, finally the pure precipitate remains at the bottom of the container together with a small amount of washing fluid. *Sedimentation* means that the precipitate settles out of the fluid to the bottom of the container via the force of gravity.

The phases separated by filtration are called *precipitate* (solid) and *filtrate* (liquid). If the hydrostatic pressure of the mixture promotes the flow of the liquid, it is called simple *filtration*; if the reduced pressure promotes the flow of the liquid, it is

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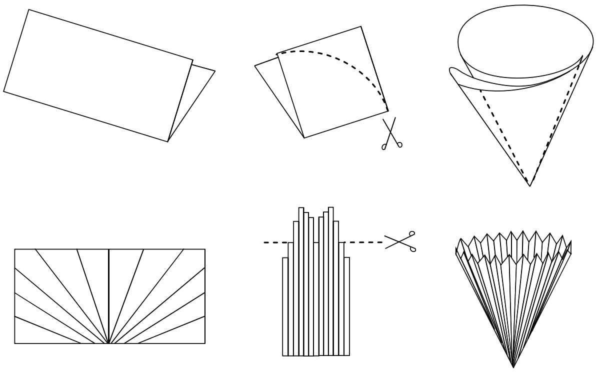
called *vacuum filtration*. In the case of filtration at atmospheric pressure, we usually use a normal, conical short-stemmed *funnel*; in the case of vacuum filtration, a *Büchner funnel* or *sintered glass funnel* is used.

Porous filter materials are used for filtration; most frequently it is a filter paper. The filter papers are available in the form of sheets or cut into a circle shape. A circular filter paper corresponding to the funnel is prepared from a sheet of filter paper in that way, that the funnel is placed on the sheet with rim downwards, circled, and cut out.

The preparation of a *conventional filter paper* (Figure III-20.) is as follows: the round filter paper is folded in four, cut to be round and placed into the funnel. Before the filtration, the filter paper should be humidified with the solvent and stuck to the funnel with a glass rod or you clear finger. In this case, there will be no air between the paper and the wall of the funnel.

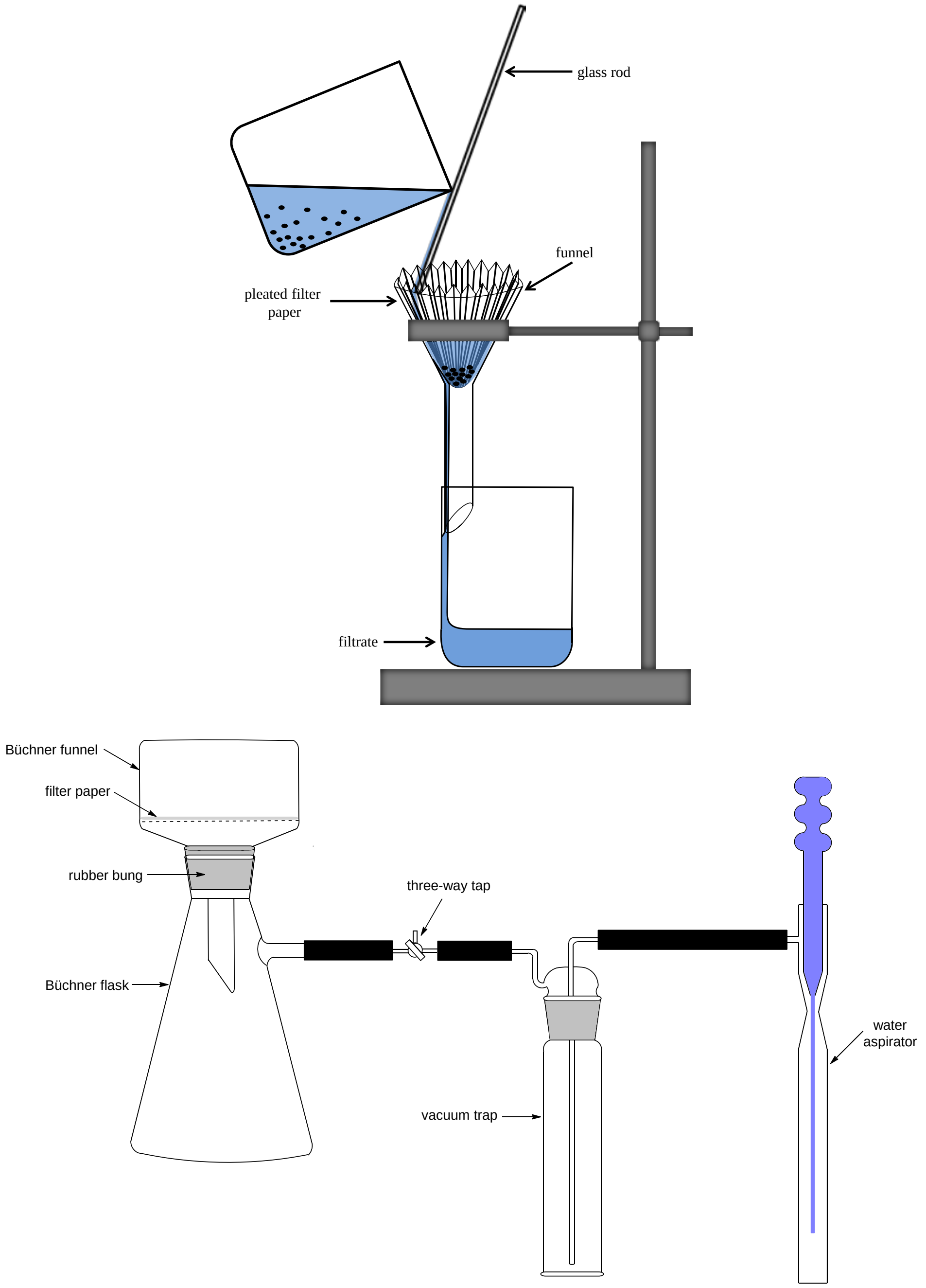
**Figure III-20:** How to prepare conventional and pleated filter paper.



When preparing a *pleated filter paper*, fold the round filter paper in eight, unfold the last two steps, and fold each eights of the circle in three (Fig. III-20.). Open the filter paper completely, and place it into the funnel. When pouring the liquid, press the filter paper gently into the funnel.

During filtration, the funnel is placed to a laboratory ring fixed to a retort stand (Figure III-21.).

**Figure III-21:** Filtration at atmospheric pressure and under vacuum



During filtration at atmospheric pressure (Figure III-21; a), the following should be taken care:

a. The edge of the filter paper should be at least 0.5 cm over the rim of the funnel.
b. The stem of the funnel should touch the side of the container, because the continuous flow of the liquid speed up the filtration.
c. The liquid should be introduced into the funnel with the help of a glass rod.
d. The level of the liquid in the funnel should be kept at least 0.5 cm lower than the edge of the filter paper.

If we would like to speed up the filtration or more completely separate the precipitate and the filtrate, we can decrease the pressure under the funnel by aspiration.

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The porcelain Büchner funnel is used in simple cases of filtration under vacuum; the filter paper is placed to the perforated plate. The apparatus consists of a Büchner flask, a vacuum trap, and a water aspirator (Fig. III-21; b).

#### III.5.1.1 Experimental task: Separation of components of a powder mixture containing calcium carbonate and sodium chloride

Determine the ratio of the components (and express in m/m %) in a powder mixture containing solid calcium carbonate and sodium chloride in an unknown ratio. The process is as follows:

1. Measure a known amount of the mixture (5-10 grams) into a 100 $cm^3$ beaker using an analytical scale.
2. Prepare a pleated filter paper of appropriate size for filtration, and measure its weight with an analytical scale.
3. Pour freshly boiled hot distilled water to the mixture in such an amount that it should be able to dissolve the total amount of the sodium chloride. The required amount of water should be estimated as if the whole mixture would be sodium chloride. The solubility of sodium chloride (g NaCl/100 g $H_2O$) is as follows:

| | | | |
|---|---|---|---|
| 273 K | 35.6 | 333 K | 37.0 |
| 293 K | 35.8 | 353 K | 38.0 |
| 313 K | 36.4 | 373 K | 39.2 |

4. The sodium chloride solution should be decanted from the insoluble calcium carbonate, which settles down, and the remaining calcium carbonate should be decanted until the filtrate remains clear after addition of silver nitrate solution. Then filter the insoluble calcium carbonate through the previously tarred filter paper.
5. Place the filtrated precipitate into a porcelain dish together with the filter paper, dry it in a heating chamber at 110ºC, and measure it. Dry it again for 20 minutes, and measure its weight again. If the weight did not change, the precipitate can be considered as dry.
6. When you know the weight of the mixture and the calcium carbonate, you should be able to calculate m/m% composition of the mixture.

### III.5.2 Drying

*Drying* is a process, during which the liquid – usually water –, which is absorbed at the surface and in the inner part of solids with different strengths, is removed. The method of drying depends on the characteristics of the material, that should be dried, and the desired degree of drying.

Usually such kind of materials is *air-dried at room temperature*, which degrade or lose more water than required, when dried with a dehydrating agent or heating. These substances are dried on filter paper or watch glass. This drying method can only be used, if the aim is to reach the “air-dry” state.

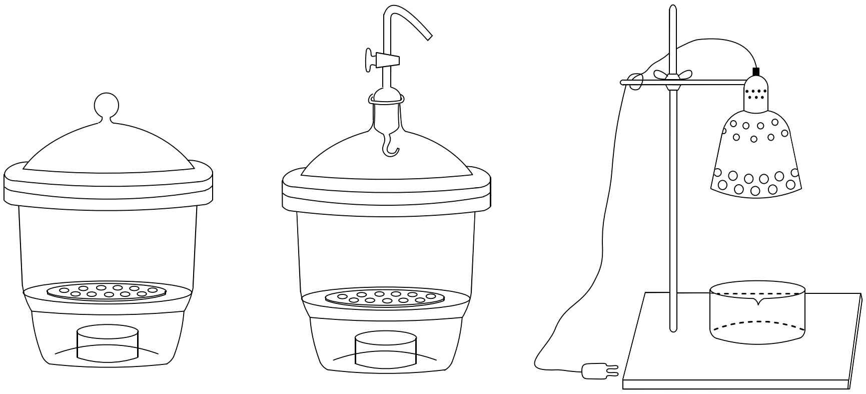
The process can be sped up by *heating*. If our substance can be heated, it is recommended to use an *electric heating chamber*, where the heat levels can be regulated automatically between 40 and 260 ºC. The laboratory samples are usually dried to constant weight at 110 ºC for preparation of the analysis. The *infrared lamp*

(Figure III-21) is frequently used for drying small amounts of solids by heating. Take care, that only thermostable substances can be dried by heating.

A *desiccator* (Figure III-22; a, b) is used for drying with *desiccants*. The lower compartment of the thick-walled glass vessel contains the hygroscopic desiccant, which can be anhydrous $CaCl_2$, CaO, cc. $H_2SO_4$, KOH, $P_2O_5$, or silica. (*Anhydrous cobalt chloride* is added to the silica; therefore it has *blue* colour. The cobalt chloride acts as an indicator; if it absorbs water, it becomes purple. After this colour change, the silica cannot be used further as a desiccant, but its regeneration is possible at 100-120 ºC.) The container, which contains the substance, is put in the upper compartment of the desiccator. The ground-glass rim of the desiccator lid must be greased with a thin layer of a lubricant, which ensures an airtight seal. For speeding up drying, the desiccator can also be evacuated.

*Liquids* can be dried with drying agents, which bind the water chemically. The most frequently used drying agents include metallic sodium, metallic calcium, anhydrous $CaSO_4$, $Na_2SO_4$, active $Al_2O_3$, KOH, BaO, CaO, and $K_2CO_3$. The drying agents used for drying *gases* are usually the same as in the case of liquids.

**Figure III-22:** Desiccators and infrared lamp



## III.5.3 Crystallization and recrystallization

Crystallization can be used both for production and purification of compounds. A simple crystallization aims at the isolation of different compounds, while the so-called recrystallization is used for the purification of the isolated crystalline compounds. For crystallization, a supersaturated solution of the crystallized material should be prepared, e.g. with cooling of a hot saturated solution, concentration of an unsaturated solution, or changing the composition of the solvent of the nearly saturated solution. Crystal nuclei start to develop in the supersaturated solution, on which the dissolved particles can precipitate, and the impurities remain in the solvent, or do not dissolve at all.

The size of the crystals depends on the relation between the development of crystal nuclei and speed of crystal growth. The faster the rate of cooling, the smaller the crystals form; in this case numerous small crystals form. The slower the rate of cooling, the larger the speed of the crystal formation is; in this case fewer big crystals form.

If the crystallization is difficult to start (the nuclei do not start to develop), the process can be successfully promoted by rubbing the inner surface of the container, or *putting a few grains of the seed crystal* into the supersaturated solution.

If crystallization aims at purification, the process is called *recrystallization*: the substances are dissolved, and crystallized again. Recrystallization can be used for purification of such compounds, whose solubility changes with temperature more than those of the impurities. The solubility of the majority of water-soluble substances increases with temperature; therefore a hot saturated solution should be prepared for their recrystallization. To improve the effectiveness of the purification, a so-called activated carbon with high surface area is added to the hot saturated solution. This activated carbon is able to adsorb impurities on its surface (usually with the help of van der Waals forces) (*flocculation*). If the filtered hot solution is cooled, it becomes supersaturated, and crystals of the substance start to form. The remaining cool solution is called the *mother liquor*; it is saturated with the crystallized substance and keeps the soluble impurities of the crystallized material in solution.

Some practical aspects of recrystallization:

1. The temperature of the hot saturated solution should be at least with 10-20 ºC below the boiling point of the solvent.
2. The hot saturated solution should be filtered through pleated filter paper with the help of a preheated funnel.
3. The crystals can be filtered at atmospheric pressure using conventional filter paper, or under vacuum using a Büchner funnel or a sintered glass funnel.
4. The mother liquor should be washed from the surface of the filtered crystals with a small amount of cold solvent.
5. The impurities adsorbed at the surface of the crystallized substances can be removed with clarifying agents or recrystallization.

### III.5.3.1 Calculation examples for recrystallization

1. Prepare a saturated solution of $KNO_3$ at 75 ºC by dissolving 90.0 g of $KNO_3$ in water, and cool the solution to 20 ºC. Calculate the mass (in g) of the deposited $KNO_3$. What is the yield of recrystallization? Concentration of the saturated solution of $KNO_3$ is 150.0 g $KNO_3$/100 g water at 75 ºC, and 32.0 g $KNO_3$/100 g water at 20 ºC.

| | | |
|---|---|---|
| at 75 ºC | 150.0 g $KNO_3$ | in 100.0 g water |
| | 90.0 g $KNO_3$ | in x g water |

$$x = \frac{90.0 \cdot 100.0}{150.0} = 60.0 \text{ g}$$

| | | |
|---|---|---|
| at 20 ºC | in 100.0 g water | 32.0 g $KNO_3$ |
| | in 60.0 g water | x g $KNO_3$ |

$$x = \frac{60.0 \cdot 32.0}{100.0} = 19.2 \text{ g}$$

The mass of $KNO_3$ deposited on cooling is 90.0 - 19.2 = 70.8 g.

The yield:

$$\frac{70.8 \cdot 100.0}{90.0} = 78.7\ \%$$

*Thus, 70.8 g of $KNO_3$ will be deposited. The yield of recrystallization is 78.7 %.*

2. What a mass (in g) of $CuSO_4 \cdot 5\ H_2O$ will be deposited if 200.0 g of 40 m/m% $CuSO_4$ solution is cooled to 30 ºC. Concentration of the saturated solution at 30 ºC is 20 m/m%. ($M(CuSO_4) = 159.6$ g/mol; $M(CuSO_4 \cdot 5\ H_2O) = 249.6$ g/mol)

$$\text{Mass of the dissolved material in 200 g solution} = \frac{200.0 \cdot 40}{100} = 80\ \text{g}$$

Mass of the deposited $CuSO_4 \cdot 5\ H_2O$ = x g

$$\text{Mass of } CuSO_4 \text{ in x g } CuSO_4 \cdot 5\ H_2O = \frac{x \cdot 159.6}{249.6} = 0.639 \cdot x\ \text{g}$$

Mass of $CuSO_4$ remaining in the solution = (80.0 – 0.639 x) g

Mass of the solution = (200.0 – x) g

$$(200.0 - x) \cdot 0.2 = 80.0 - 0.639\ x$$

$$x = 91.11$$

*Thus, 91.1 g of $CuSO_4 \cdot 5\ H_2O$ will be deposited.*

### III.5.3.2 Experimental task: Purification of benzoic acid with alkaline precipitation and recrystallization

Measure 1.0 g of benzoic acid (technical grade) on an analytical scale into a 50 $cm^3$ Erlenmeyer flask. Add 5 $cm^3$ of sodium hydroxide solution and shake until it will dissolve. If it does not dissolve completely at room temperature, you can mildly warm it through asbestos wire gauze.

Filter the cool (or cooled) sodium benzoate solution, which still can contain insoluble impurities, into a 10 $cm^3$ beaker. Add a pinch of activated carbon to the filtrate and mix it well (see flocculation). Filter the suspension again into a 10 $cm^3$ beaker. While vigorously stirring the mixture with a glass rod, gently pour 1 $cm^3$ of concentrated hydrochloric acid to the filtrate.

Filter the white curdy precipitate through Büchner funnel under vacuum. Tamp down well the precipitate with a flat-ended glass rod and wash it with 5 $cm^3$ of ice-cold water with which the beaker contained the precipitated benzoic acid has been washed.

Transfer the filtered material into a 50 $cm^3$ Erlenmeyer flask with the help of a spoon and a glass rod. Wash the adhered benzoic acid from the funnel, the spoon, and the glass rod into the Erlenmeyer flask with about 15-20 $cm^3$ distilled water.

Warm the solution through asbestos wire gauze. When the solid completely dissolved, filter the hot solution into another 50 $cm^3$ Erlenmeyer flask. Allow the solution to cool to room temperature until crystals start to form. Then put the flask into an ice-cold water bath. Filter the crystalline benzoic acid by means of a water aspirator and wash it with a small amount of ice-cold distilled water. Continue aspiration until water no longer drips from the funnel.

Spread out the substance on a filter paper and allow to dry. When it is completely dry, weigh it together with the filter paper. Put the pure substance into a watchglass, and measure the weight of the filter paper. Calculate the loss of recrystallization process.

### III.5.3.3 Purification of contaminated alum with recrystallization

Contaminated crystalline materials can be purified by recrystallization if solubility properties of the substance and its impurities make it possible.

If impurities are present in only a few percent, and solubility of the compounds is similar, the procedure as follows: Prepare a saturated solution of the substance at an elevated temperature. Then cool down the solution, in order to get a supersaturated solution. Wait for precipitation of the crystals, then filter and dry them. In the following experiment crystalline alum ($KAl(SO_4)_2 \cdot 12\ H_2O$) contaminated with 5 m/m% copper sulphate ($CuSO_4 \cdot 5\ H_2O$) and 1 m/m% insoluble substance (quartz) will be purified by recrystallization.

Measure 30 g of contaminated alum on analytical scale. Suspend it with 30 $cm^3$ of distilled water and warm up to boil to dissolve alum and copper(II) sulphate. Filter the hot solution through pleated filter paper using a preheated funnel. Cool the Erlenmeyer flask (containing the filtrate) with tap water and filter the precipitated crystals with a conventional filter paper. Wash the filtered crystals with 2-3 $cm^3$ of cold distilled water to remove the adsorbed copper(II) sulphate. Transfer the crystals into a 50 $cm^3$ Erlenmeyer flask and dissolve the crystals in a minimum amount of boiling water. Allow the solution to cool to room temperature until crystals start to form. Then put the flask into an ice-cold water bath. Filter the crystalline alum by means of a water aspirator and wash it with a small amount of ice-cold distilled water. Continue aspiration until water no longer drips from the funnel.

Spread out the substance on a filter paper and allow to dry. When it is completely dry, weigh it together with the filter paper. Put the pure substance into a watchglass, and measure the weight of the filter paper. Calculate the yield of recrystallization process.

### III.5.4 Distillation, sublimation

Distillation is a process, during which a liquid is evaporated and the vapour is condensed and captured in another flask. The product of the process is called distillate.

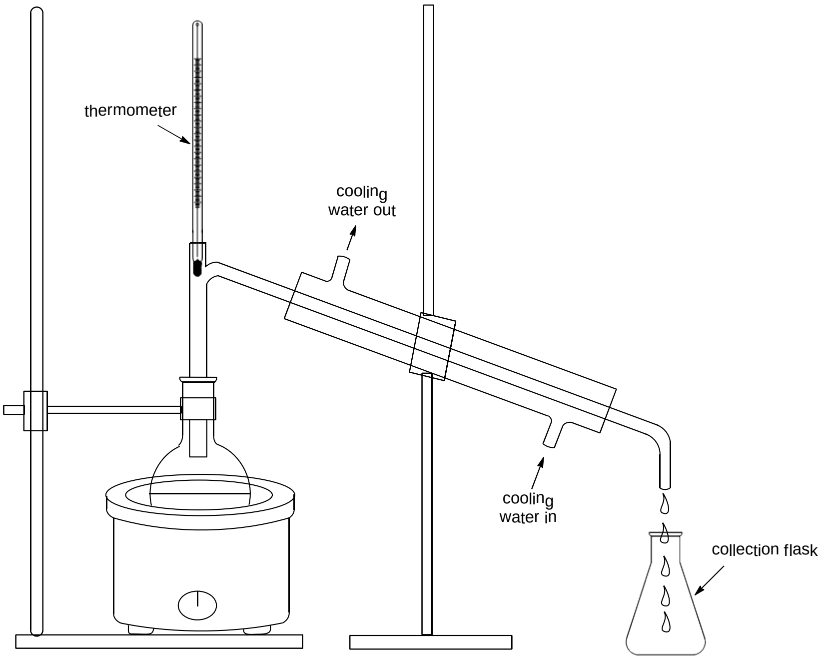
*Distillation aims at:*

a. separation of a liquid from non-volatile solids, or
b. separation of liquids having different boiling points.

Distillation is a method of separating mixtures based on differences in composition of the liquid mixture and its vapour formed at a certain temperature – unless it is an azeotropic mixture. This method is suitable for separation of volatile and non-volatile compounds and for separation of volatile compounds having different boiling points.

A simple distillation apparatus can be seen on Figure III-23. The vapour forms in the distilling flask and it is liquefied again in the *Liebig condenser*, which leads into the collection flask. The *Kugelrohr* and the *coil condenser* have larger cooling surface area, but they must be vertically arranged, otherwise the distillate cannot pass through consistently.

**Figure III-23:** A simple distillation apparatus



Before heating, a few pieces of boiling stone, glass beads, unglazed porcelain, or glass capillary should be placed into the distilling flask to promote boiling. These materials prevent delay of boiling, during which the sudden excessive bubble formation may result in rupture of the distilling flask.

The method of heating depends on the boiling point and flammability of the solution. E.g. in the case of a flammable solution, whose boiling point is under 100 ºC, a water bath should be used. The method of cooling is as follows: in the case of solutions, whose boiling point is under 120 ºC, a tap water is circulated in the cooler; when the boiling point of the solution is between 120 and 160 ºC still water is used for cooling; while above 160 ºC, the condenser is air-cooled.

Some compounds (e.g. camphor, arsenic) turns to gas when heated without turning into a liquid first at atmospheric pressure. This phenomenon is called *sublimation*, and its cause is that pressure is above the atmospheric pressure at the triple point of the substance. Sublimation can also be used for purification of substances.

### III.5.4.1 Experimental task: Fractional distillation of a methanol-water mixture

Pour 50 cm$^3$ methanol and 50 cm$^3$ distilled water into a 250 cm$^3$ distilling flask. Add a few pieces of boiling stone to the mixture to promote boiling and join the distilling flask to the distilling head. Ensure that the ground glasses are aligned properly, then open the tap of the cooling water and turn on the heating (in the case of flammable solutions, a closed electric heater must be used!). When boiling starts, adjust the heating so that one drop of the distillate can get into a graduated cylinder in every 1-2 seconds. Read the temperature, and plot the boiling curve initially after every 10 cm$^3$ than later after every 5 cm$^3$.

Read the temperature, when the distillation starts (when the first drop drops into the graduated cylinder). Read the temperature after every 5 cm$^3$ of distillate. Continue the distillation, until 80 % of the solution distils. Take care not to overheat the system.

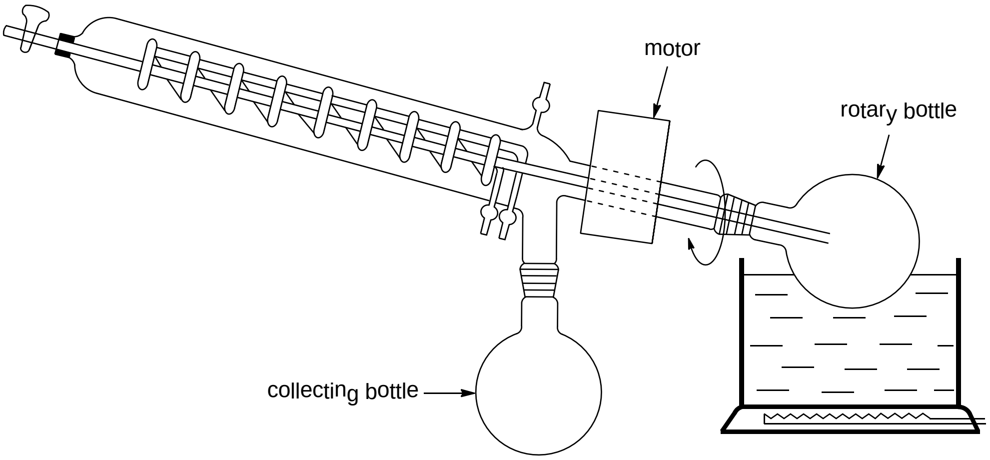
In the case of a proper distillation, the end of the thermometer is always wet because of the precipitated vapours. The evaporation of the whole solution from the distilling flask is forbidden. After the stop of heating, allow the cooling water to circulate for some minutes.

### III.5.5 Evaporation

*Evaporation* of a small amount of volatile solutions can be managed in evaporating and crystallization dishes, glass beaker having wider mouth, watch glass, or porcelain dish under a chemical fume hood. A *water bath* is usually used for evaporation of bigger amounts of solutions, which heats the solution to 80 ºC, and so the flask does not rupture.

A *vacuum evaporator* is used for the evaporation of larger amounts of flammable and expensive solvents. The evaporation can be sped up, if the vapour of the solvent is removed from the air space of the flask. *Vacuum rotary evaporators* are highly effective tools of removal of the majority of solvents under vacuum. The high effectiveness of this equipment results from the fact that the constantly moving rotary bottle ensures big surface for evaporation, and the constantly renewing liquid film evaporates well (Figure III-24).

**Figure III-24:** Rotary vacuum evaporator



### III.5.6 Freeze-drying (lyophilisation)

*Freeze-drying* or *lyophilisation* is a special type of evaporation, and it means gentle, low temperature dehydration. This technique is essential for some medical and biochemical laboratory techniques. Its concept is very simple: ice sublimates at 4 kPa pressure and -50 ºC. A thin layer of solution is frozen to the side of the container, and the container is evacuated. The frozen water sublimates due to the vacuum; therefore the system remains cool even after the cessation of the outer cooling. The evaporated vapour is somehow bond (in this case by freeze). It is a very gentle method, because the system is so cooled that our samples (e.g. the heat sensitive proteins, antibiotics, microorganisms) are not exposed to heat; there is no foaming, the volatile compounds remain in the sample, risks of microbial and enzymatic degradation as well as oxidative damage are minimal. There is no volume reduction; the result of the process is a fine, porous material with high surface area, which is easily soluble again.

# IV Gas Laws

## IV.1 The gas state

Depending on the temperature and pressure, matters can exist in three fundamental states: *solid, liquid and gas states*. (Some materials do not occur in all states under common conditions.) The stability of different phases determined by *macroscopic state variables* (temperature, pressure) can be learned from the *phase diagrams*. In different states of a chemically uniform material the distance between the particles, the kinetic energy of the particles and the magnitude of attractive forces (vectorial sum of the attractive and repulsive forces) between the particles are also different.

In the gas state, (in the case of ideal gases) there are no intermolecular interactions between the particles (atoms, molecules) and the distribution of particles (atoms, molecules) is completely random. Gases share the common features of

- being compressible;
- having low density; and
- expanding on increasing volume.

The gas state of a chemically uniform material can be definitely characterized by three macroscopic state variables:

- volume ($V$);
- pressure ($p$); and
- temperature ($t$).

The three *state variables* are not independent from each other: for example, the volume of given amount of gas is clearly determined by the pressure and temperature of the gas. The correlation between state variables is called *state equation*, which is usually different for each substance. However, if the pressure is small enough and the temperature is quite high, the same state equation is valid for each gaseous substance. This state is called as *ideal gas state*. The ideal gas state is the limit state of the gases; the smaller the pressure the more approached.

### IV.1.1 The combined gas law

Between the three state variables of a given amount of ideal gases the following correlation can be observed:

$$p \cdot V = p_0 \cdot V_0 \, (1 + \alpha \cdot t) \tag{1}$$

where:

$p_0$ and $V_0$ are the pressure and the volume of the given quantity (mole) of the gas at a temperature of 0 °C.

$\alpha \, (\frac{1}{273.15})$ is the *coefficient of thermal expansion*, which is the same value for each gas.

The above correlation (referred to as the combined gas law) involves *Boyle's* and *Mariotte's* as well as *Gay- Lussac's* laws. The *combined gas law* expresses that

- the pressure of given amount of gas at constant temperature is inversely proportional to the volume of the gas (*Boyle's* and *Mariotte's law*);
- the volume of given amount of gas at constant pressure expands with the $\frac{1}{273.15}$th part of its volume measured at 0 °C if the temperature of the gas is increased by 1 °C (*Gay-Lussac's law*);
- the pressure of given amount of gas at constant volume increases with the $\frac{1}{273.15}$th part of its pressure measured at 0 °C if the temperature of the gas is increased by 1 °C (*Gay-Lussac's law*).

### IV.1.2 Avogadro's law

It is an important property of the ideal gases that in their equal volumes - at the same pressure and temperature - equal number of particles (atom, molecule) can be found. Consequently, equal volumes of all gases - at the same temperature and pressure - have the same number of molecules (*Avogadro's law*). Based on experiments, the molar volume of ideal gases is $V = 22.412$ dm$^3$ at 0 $^{o}$C temperature and 101.325 kPa (1 atm) pressure. This conditions ($t$ = 0 $^{o}$C; $p$ = 101.325 kPa) is called *normal conditions*.

The combined gas law can be simplified considering *Avogadro's law* and expressing the temperature compared to that of the so called absolute zero temperature, which is equal to -273.15 $^{o}$C.

According to equation (1) the $p \cdot V$ product of ideal gases would become zero at -273.15 $^{o}$C. Accordingly, lower temperature than -273.15 $^{o}$C cannot be reached. The $t$ = -273.15 $^{o}$C is the *natural zero point* of the temperature scale (so called *absolute zero point*). Recognizing importance of the absolute zero point, Kelvin instituted the thermodynamic temperature scale ($T$), which is an absolute scale with $T$ = 0 as the lowest point. Temperatures above $T$ = 0 are then most commonly expressed by using the Kelvin scale, in which gradations of temperature is called *kelvin* (K). 1 K corresponds to the same temperature difference like 1 $^{o}$C. The correlation between the Kelvin scale and the Celsius scale as it follows:

$$T = (t + 273.15)\ K \qquad (2)$$

where:

$T$ is the thermodynamic temperature expressed in kelvin (K);
$t$ temperature expressed in degrees Celsius ($^{o}$C)

When the temperature expressed in $^{o}$C is replaced by the temperature expressed in K ($t = T$-273.15) in equation (1) equation (3) is obtained:

$$p \cdot V = p_0 \cdot V_0 \left(1 + \frac{T - 273.15}{273.15}\right) = p_0 \cdot V_0 \frac{273.15 + T - 273.15}{273.15} \qquad (3)$$

If the melting point of ice expressed in K is called $T_0$ ($T_0$ = 273.15 K), equation (3) is transformed to the following formula:

$$p \cdot V = \frac{p_0 V_0}{T_0} T \tag{4}$$

The state equation with respect to 1 mole of gas (molar volume marked in capital letters) can be written as:

$$p V_m = \frac{p_0 V_{m(0)}}{T_0} T \tag{5}$$

Generalizing, we get the following formula:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \tag{6}$$

### IV.1.3 The general gas law

Applying the combined gas law for 1 mole of ideal gas we can define a universal constant:

$$R = \frac{p V}{T} = \frac{p_0 V_0}{T_0} \tag{7}$$

where:

$p_0$ = 101.325 kPa (1 atm),
$V_0$ = molar volume of gases under normal conditions: 0.022414 $m^3$/mol; and
$T_0$ = 0 $^oC$ = 273.15 K

$$R = \frac{101.325\,\mathrm{N/m^2} \cdot 22.4142 \cdot 10^{-3}\,\mathrm{m^3/mol}}{273.15\,\mathrm{K}} = 8.314\,\mathrm{Nm/K \cdot mol}$$

Using $R$, the *universal gas constant*, general correlation can be given between the pressure, volume, temperature as well as mole number of ideal gases:

$$p \cdot V = n \cdot R \cdot T \tag{8}$$

where:

$p$ = pressure of the gas,
$V$ = volume of the gas,
$n$ = mole number of the gas,
$R$ = universal gas constant, and
$T$ = thermodynamic temperature (K).

The *general gas law* states that multiplication of pressure and volume of a given amount of ideal gas is directly proportional to the absolute temperature; and it is independent of the nature of the gas particles.

In the case of real (non-ideal) gases the $p \cdot V$ product (at constant temperature) varies depending on the nature of particles and the pressure of the gas.

### IV.1.4 Dalton’s law

The pressure of gas mixtures is caused by collision of different gas particles and the wall of the container. Based on this, a *partial pressure* can be defined for each component of the mixture. Because there is no interaction between the particles (ideal gas mixture), the total pressure exerted by a mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases at the same temperature and pressure.

*Dalton’s law* says that the total pressure of the gas mixture ($p_t$) is equal to the sum of the partial pressures of the components in the gas mixture:

$$p_t = p_A + p_B + p_C + \ldots + p_X \tag{9}$$

Since the pressure – so the partial pressure too – is proportional to the number of the particles (atoms, molecules), the partial pressure of one component of the mixture is proportional to the mole fraction of the mentioned component:

$$p_A = x_A \cdot p_t$$

where:

$p_t$ = the total pressure of the gas mixture,
$p_A$ = the partial pressure of the A component, and
$x_A$ = the mole fraction of the A component.

## IV.2 Calculations

1. A gas fills 500.00 $cm^3$ of the place at a temperature of 100 °C and a pressure of 100.26 kPa. Calculate the volume of the gas under normal conditions.

   Normal conditions are specified as 0 $^oC$ and 101.325 kPa. Applying the combined gas law:

   $$V_0 = \frac{p \cdot V \cdot T_0}{p_0 \cdot T}$$

   $$V_0 = \frac{100.26 \cdot 500.00 \cdot 273.15}{101.325 \cdot 373.15} = 362.16\ \mathrm{cm}^3$$

   *Thus, the volume of the gas is 362.16 $cm^3$.*

2. An air pump sucks in 1.50 $dm^3$ of air; its pressure is 101.325 kPa. After compression the volume of the air is 250.00 $cm^3$. What pressure is needed for this if the change of temperature is neglected?

   $$\frac{p_1 \cdot V_1}{T_1} = \frac{p_2 \cdot V_2}{T_2}$$

   $$p_2 = \frac{p_1 \cdot V_2 \cdot T_2}{V_2 \cdot T_1} = \frac{101.325 \cdot 1.50}{0.25} = 607.95\ \mathrm{kPa}$$

   *Thus, it is 607.95 kPa pressure needed to reach the compression.*

3. In a gas bottle there is a gas of 16.20 MPa pressure and 300 K temperature. Calculate the pressure of the gas in the bottle after releasing 25 % of the gas, while the temperature decreases to 280 K.

   The gas remaining in the bottle is the 75 % of the original amount, which occupied the 75 % of the place in the bottle. Accordingly, the status indicators of the initial state of the gas:
   $p_1$ = 16.20 MPa
   $V_1$ = 0.75 V, where V = the volume of the bottle
   $T_1$ = 300 K

   State parameters of the final state of the gas:

   $p_2$ = ?
   $V_2$ = V
   $T_2$ = 280 K

   Using the general gas law:

$$p_2 = \frac{p_1 \cdot V_2 \cdot T_2}{V_2 \cdot T_1} = \frac{16.20 \text{ MPa} \cdot 0.75\, V \cdot 280 \text{ K}}{V \cdot 300 \text{ K}}$$

$$p_2 = 11.34 \text{ MPa}$$

   *Thus, the pressure of the gas remained in the bottle is 11.3 MPa.*

4. What size of container should be connected to a 50.00 $dm^3$ gas bottle containing a gas of 10.132 MPa pressure if we want the pressure of the gas in both tanks to be 506.60 kPa?

   Applying combined gas law, the volume of the gas under the new conditions can be calculated:

$$V_2 = \frac{p_1 \cdot V_1}{p_2} = \frac{50.00 \text{ dm}^3 \cdot 10.132 \text{ MPa}}{0.5066 \text{ MPa}} = 1000 \text{ dm}^3$$

$$\Delta V = 950 \text{ dm}^3$$

   *Thus, a 950 $dm^3$ container should be connected to the gas bottle.*

5. Calculate the mass of 1.00 $dm^3$ of nitrogen gas under normal conditions.

a. According to *Avogadro's law*:

   The molar volume of the gas under normal conditions 22.41 $dm^3$.
   Thus,

| | |
|---|---|
| the volume of 28.01 g of nitrogen is | 22.41 $dm^3$ |
| x g | 1.00 $dm^3$ |

$$x = \frac{28.01 \text{ g} \cdot 1.00 \text{ dm}^3}{22.41 \text{ dm}^3} = 1.25 \text{ g}$$

b. According to the *general gas law*:

$$pV = nRT = \frac{m}{M}RT$$

$$m = \frac{p \cdot V \cdot M}{RT}$$

$$m = \frac{101325\,\mathrm{N} \cdot \mathrm{m}^{-2} \cdot 10^{-3} \cdot \mathrm{m}^3 \cdot 28.01\ \mathrm{gmol}^{-1}}{8.314\,\mathrm{N} \cdot \mathrm{m} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1} \cdot 273.15\ \mathrm{K}} = 1.25\ \mathrm{g}$$

*Thus, the mass of 1.00 dm*$^3$ *of nitrogen gas is 1.25 g under normal conditions.*

6. The mass of 1.00 dm$^3$ carbon dioxide gas is 1.977 g under normal conditions. At what pressure will the mass of 1.00 dm$^3$ of carbon dioxide gas be 1.00 g, if the temperature is kept constant?
7. The volume of 2.00 g of monoatomic gas is 1.39 dm$^3$ at a pressure of 810.6 kPa and at a temperature of 0 $^o$C. What is the atomic mass of the gas? What is the nature of the gas?
8. A gas mixture is consisted of 2.00 g of hydrogen and 10.00 g of methane. The total pressure of the mixture is 253.31 kPa. Calculate the partial pressure of methane.
9. The pressure of a gas is 98.90 kPa at a temperature of 0 $^o$C. How does the pressure vary if the temperature is increased to 15 $^o$C and the volume is not changed?
10. In a gas tank there is a gas of 27 °C temperature and 4.053 MPa pressure. Calculate the pressure if 25 % of the gas is released and the temperature is decreased to 7 °C.
11. The volume of a gas is increased threefold. Calculate the temperature of the gas if the pressure is kept constant.
12. Air contains 21.0 V/V % oxygen and 79.0 V/V % nitrogen. What is the partial pressure of oxygen under normal conditions? Calculate the average molar mass of air.
13. 3 dm$^3$ of nitrogen gas of 96.00 kPa pressure is mixed with 2 dm$^3$ of oxygen gas. The volume of the mixture is 5 dm$^3$, its pressure is 97.59 kPa. Calculate the original pressure of the oxygen gas.
14. A 3.0 dm$^3$ gas tank and a 4.0 dm$^3$ gas tank are connected by a bartender tube. Initially, the 3.0 dm$^3$ gas tank contains oxygen of 56.0 kPa pressure and the 4.0 dm$^3$ tank contains oxygen of 103.6 kPa pressure. Temperature of the gases is equal in the two tanks. Calculate the pressure in the tanks after the tap is opened.
15. A compound is composed of 54.5 m/m% of carbon, 36.4 m/m% of oxygen and 9.1 m/m% of hydrogen. Volatilizing 0.1963 g of the compound 115.90 cm$^3$ of 35 °C gas with a pressure of 99.20 kPa is formed. Calculate the empirical formula of the compound.

# V Concentrations, dilution and mixing solutions

The multicomponent homogenous (single-phase) systems are called solutions and mixtures. In *mixtures* the amounts of the components are approximately equal. In *solutions* the amount of one component (solvent) is greater than the amount of the other (or further) component(s). The monophasic homogenous mixtures of substances may be solid, liquid or gas state. The multicomponent homogenous systems in gas state are usually referred to as *mixtures*. In laboratory practice the liquid solutions are the most important.

Concentration is the ratio of the quantities of solute and solution. The quantity of solute and solution can be specified with the mass, the mole number or the volume. Accordingly, several units of concentration can be defined.

- **Mass fraction ($\omega$) and mass percent (*m/m%*)**

If the quantity of both solute and solution is given in mass unit, we can calculate the mass fraction ($\omega_i$). Mass fraction defines the mass of the substance per unit mass of the solution:

$$w_i = \frac{m_i}{\Sigma m_i}$$

where $m_i$ is the mass of *i*th component of the mixture. Multiplying *mass fraction* by 100 gives the mass percentage, which is the number of the grams of the component in 100 g solution. Mass percentage is signed by *m/m%*. The sum of particular mass fractions of a solution is equal to 1. The sum of particular mass percentages of a solution is equal to 100.

- ***Mole fraction and mole percent (n/n%)***

If quantity of both the solute and the solution is given in mole, *mole fraction* can be calculated. Multiplying mole fraction by 100 gives the *mole percent ($x_i$ or mole%).*

$$x_i = \frac{n_i}{\Sigma n_i} = \frac{m_i / M_i}{\Sigma m_i / M_i}$$

To calculate mole fraction and mole percent we should know the *number of moles* (*n*) of each component. It can be calculated by dividing mass of *i*th component ($m_i$) by molar mass of the component ($M_i$):

$$n_i = \frac{m_i}{M_i}$$

Mole fraction of one of the components in a solution can be calculated by dividing number of moles of the particular component by the total number of moles in the solution.

If the solution consists of two components, $x_1$ and $x_2$ are the mole fractions:

$$x_1 = \frac{n_1}{n_1 + n_2} \qquad x_2 = \frac{n_2}{n_1 + n_2}$$

The sum of particular mole fractions of a solution is equal to 1. The sum of particular mole percents of a solution is equal to 100.

- **Volume fraction (*f*) and volume percent (*V/V%)***

*Volume fraction* and *volume percent* are only meaningful if mixing of components of a solution is not accompanied by volumetric change. For example, these relationships can be applied for mixtures of ideal gases:

$$V = \Sigma V_1$$

where $V_i$ = volume of the *i*th component at a given temperature and pressure.

In the case of gases volume percent is equal to mole percent, therefore the composition of gases is usually given in volume percent. So, volume percent specifies the volume of a given component in 100 $cm^3$ solution (or mixture). Its symbol is *V/V%.*

- **Mass concentration (γ) and mass per volume percent (*m/V%*)**

In the case of mass concentrations the amount of the solution is given with its volume. *Mass concentration* (γ) is the amount of solute which is dissolved in 1 $dm^3$ of solution. For example, 50 g of NaCl in 1 $dm^3$ of NaCl solution. *Mass per volume percent* (*m/V%*) gives the mass of solute in 100 volume units of solution (or mixture). For example, 100 $cm^3$ of 35 m/V% solution contains 35 g of solute, what is a tenth part of the mass concentration. This concentration unit is very often used during laboratory practice.

- **Molarity or mole concentration (*c*)**

*Molarity* (c) or *mole concentration* specifies the numbers of moles of solute in 1000 $cm^3$ of solution.

$$c = \frac{n_a}{V}$$

where:

$n_a$ = number of moles of solute,
$V$ = volume of solution (in $dm^3$).

The SI unit of molarity is $mol/m^3$, but in chemical and pharmaceutical practice the use of $mol/dm^3$ is more convenient. The $mol/dm^3$ unit is abbreviated as „M” and it is also called „*molar*”.

Mass concentrations vary depending on the temperature due to the thermal expansion of solution. Therefore, the application of them is only meaningful at constant temperature.

The reciprocal value of mass concentration is called *dilution*, which is equal to the volume of a solution that contains unit amount of solute. E.g. the reciprocal value of molarity is equal to the volume of solution ($dm^3$) that contains 1 mole of solute (*molar dilution*).

$$V_i = \frac{1}{c_i}$$

- **Molality or Raoult concentration ($c_R$)**

Concentration of dilute solutions are often expressed with their molality. *Molality* specifies the number of moles of solute in 1000 g (1 kg) of solvent. In case of dilute solutions the numerical value of molality is approximately equal to molarity. However, molality– similar to mass percentage and mole percentage – is not a volume-based concentration unit; thus its numerical value does not depend on temperature of solution.

$$c_R = \frac{n_a}{m_s}$$

where:

$n_a$ = number of moles of solute,
$m_s$ = mass of solvent (in kilogram).

- **Further concentration units**

In addition, in case of calculations related to the colligative properties of dilute solutions (e.g. cryoscopy, ebullioscopy) other concentration unit can also be used. One of the examples is that one, which determines the quantity of solute (g) in 1000 g of solvent.

In special cases *normal concentration* (normality) is used in practice of volumetric analysis. *Normality* denotes the numbers of gram equivalent mass of solute in 1000 $cm^3$ volume of solution. The unit of normality is gram equivalent/$dm^3$, which is abbreviated by „N" and it is also called „*normal*". The gram equivalent mass of a substance may vary with the type of reaction it undergoes. Although use of normality is discouraged nowadays, in articles of the VIIth edition of the Hungarian Pharmacopoeia it is generally used. Because several articles of the VIIth edition of the Hungarian Pharmacopoeia is still in power, - therefore pharmacy students perform experiments using this concentration unit - here a short description of calculation of gram equivalent mass of a compound in the most important kind of reactions is described.

- *In case of acids and bases* the gram equivalent mass is equal to the quotient of the molar mass and the number of exchanged hydrogen or hydroxide ions in the particular reaction:

$$E_m = \frac{\text{molar mass}}{\text{number of exchanged hydrogen ion/hydroxide ion}}$$

- *In case of normal salts* the gram equivalent mass is equal to the quotient of the molar mass and the product of the number and the charge of the metal ions:

$$E_m = \frac{\text{molar mass}}{\text{number of metal ions x charge of metal ions}}$$

- *In the case of redox reactions* the gram equivalent mass is equal to the quotient of the molar mass and the change of oxidation number (the number of lost or gained electrons) in the particular reaction:

$$E_m = \frac{\text{molar mass}}{\text{number of lost or gained electrons}}$$

Furthermore, “*parts per million*” (*ppm)* and “*parts per billion*” (*ppb)* concentrations are used in analytical chemistry, especially when the solute concentrations are very small (almost trace amounts). “*Parts per million*” (*ppm)* concentration determines the mass of the given component in a million ($10^6$) mass units of the mixture. For example, if a solution has 1 ppm solute this would mean that 1 g of solution would have one "millionth" gram of solute. Similarly, „*parts per billion*” (*ppb)* concentration shows the mass of the given component in a billion ($10^9$) mass units of the mixture. By definition:

$$1\ \text{ppm} = \frac{1\ \text{mg of solute}}{1000\ \text{g of solution}}$$

$$1\ \text{ppb} = \frac{1\ \mu\text{g of solute}}{1000\ \text{g of solution}}$$

- **Saturated and unsaturated solution. Solubility.**

Dissolution can be unlimited if the solute is soluble or miscible in all proportions in the solvent (e.g. mixtures of alcohol and water, sulphuric acid and water, etc.); or dissolution can be limited, when the amount of solute in a given mass/volume of solvent is limited (e.g. mixtures of phenol and water, saline and water, etc. In the latter case, saturated solution can be obtained that contains the maximum amount of solute dissolved in a solvent at a particular temperature. The term *insoluble* is often applied to poorly or very poorly soluble compounds.

Solubility is the concentration of the saturated solution at given temperature. The solubility of each compound in various solvents depending on temperature can be found in the literature. In general these data shows the mass of solute (in grams) in 100 g of solvent.

- **Mixing equation**

Diluting solutions with pure solvent or mixing solutions having the same composition (solvent and solute) but different concentrations can frequently occur among tasks to be performed in laboratory. To dilute a solution means to add more solvent without addition of more solute. Calculation of concentration of the resulted solutions is based on the additive property of masses. Therefore, during dilution and/or mixing the mass of solutes and solvents does not change. (*Law of conservation of mass.*)

Due to this law, concentration of the resulted solution obtained by mixing two solutions of the same solute and solvent can be calculated as follows:

$$m_1 \cdot c_1 + m_2 \cdot c_2 = (m_1 + m_2) \cdot c_r$$

where:

$m_1$ = mass of solution 1
$m_2$ = mass of solution 2
$c_1$ = concentration of solution 1
$c_2$ = concentration of solution 2
$c_r$ = concentration of the obtained solution

If dilution is performed, concentration of the pure solvent in respect to solute is zero; therefore the equation has got a simpler form:

$$m_1 \cdot c_1 = (m_1 + m_2) \cdot c_r$$

where:

$m_1$ = mass of the initial solution
$m_2$ = mass of the added solvent
$c_1$ = concentration of the initial solution
$c_r$ = concentration of the obtained solution

If volumes are additive during mixing (or dilution) the following equations can be used:

$$V_1 \cdot c_1 + V_2 \cdot c_2 = (V_1 + V_2) \cdot c_r$$

$$V_1 \cdot c_1 = (V_1 + V_2) \cdot c_r$$

where:

$V_1$ = volume of solution 1
$V_2$ = volume of solution 2 (or solvent)
$c_1$ = concentration of solution 1
$c_2$ = concentration of solution 2
$c_r$ = concentration of the obtained solution

## V.1 **Calculations**

1. 50.0 $cm^3$ of potassium hydroxide solution containing 14.0 g of KOH was prepared. Density of the solution is 1.22 $g/cm^3$ at 20 $^oC$. Calculate the *m/V%, m/m%*, *g/dm*$^3$ *concentrations,* as well as *molarity* and *molality* of the solution! M(KOH) = 56.1 g/mol

Calculation of m/V%:

| | |
|---|---|
| 50.0 $cm^3$ of solution | 14.0 g of KOH |
| 100.0 $cm^3$ | x g KOH |

50.0 : 100.0 = 14.0 : x
x = 28.0 g

*Thus, the m/V% concentration of the potassium hydroxide solution is 28.0 m/V%.*

Calculation of m/m%:

Since $\rho$=1.22 g/cm$^3$, mass of the 50.0 cm$^3$ solution is equal to 50.0 · 1.22 = 61.0 g

| | |
|---|---|
| 61.0 g of solution | 14.0 g KOH |
| 100.0 g | x g KOH |

61.0 : 100.0 = 14.0 : x

$$x = \frac{1400.0}{61.0} = 23.0 \text{ g}$$

*Thus, the m/m% concentration of the solution is 23.0 m/m%.*

Calculation of g/dm$^3$ concentration:

| | |
|---|---|
| 50.0 cm$^3$ of solution | 14.0 g of KOH |
| 1000.0 cm$^3$ | x g KOH |

50.0 : 100.0 = 14.0 : x

x = 280.0 g

*Thus, the g/dm$^3$ concentration of the solution is 280.0 g/dm$^3$.*

Calculation of mol/dm$^3$ concentration:

| | |
|---|---|
| 50.0 cm$^3$ of solution | 14.0 g of KOH |
| 1000.0 cm$^3$ | x g of KOH |

x = 280.0 g

| | |
|---|---|
| 56.1 g of KOH | 1 mol |
| 280.0 g of KOH | x mol |

56.1 : 280.0 = 1 : x

$$x= \frac{280.0}{56.1} =5.0 \text{ mol}$$

*Thus, the mol/dm$^3$ concentration of the solution is 5.0 mol/dm$^3$.*

Calculation of molality:

The mass of 50.0 cm$^3$ volume of the solution is equal to 50.0 · 1.22 = 61.0 g
61.0 g of the solution contains 14.0 g of KOH and 61.0 – 14.0 = 47.0 g of solvent.

| | |
|---|---|
| 47.0 g of solvent | 14.0 g of KOH |
| 1000.0 g | x g of KOH |

47.0 : 1000.0 = 14.0 : x

$$x = \frac{14000.0}{47.0} = 298.0$$

*Thus, 1000.0 g of solvent contains 298.0 g of KOH.*

| | |
|---|---|
| 56.1 g of KOH | 1 mol |
| 298.0 g | x mol |

$$56.1 : 298.0 = 1 : x$$

$$x = \frac{298.0}{56.1} = 5.3$$

*Thus, molality of the solution is 5.3 mol/kg solvent.*

2. Calculate the m/m% of the sugar solution, which was prepared by dissolving 5.0 g of sugar in 73.0 g of water?

   The mass of the solution is equal to 73.0 + 5.0 = 78.0 g

   The m/m% concentration:

| | |
|---|---|
| 78.0 g of solution | 5.0 g of solute |
| 100.0 g | x g |

$$x = \frac{100.0 \cdot 5.0}{78.0} = 6.4$$

*Thus, concentration of the solution is 6.4 m/m %.*

3. Calculate molarity and normality of a 12.5 m/V% sulphuric acid solution. $M(H_2SO_4) = 98.1$ g/mol

| | |
|---|---|
| In 100.0 $cm^3$ of solution | 12.5 g of sulphuric acid |
| 1000.0 $cm^3$ | x g |

$$x = 125.0 \text{ g}$$

| | |
|---|---|
| 1 mole of sulphuric acid | 98.1 g |
| x mole | 125.0 g |

$$x = \frac{125.0}{98.0} = 1.28$$

*Thus, molarity of the sulphuric acid solution is 1.28 M.*

The gram equivalent mass of sulphuric acid is $\frac{98.1}{2} = 49.05$ g

| | |
|---|---|
| 1 equivalent of sulphuric acid | 49.05 g |
| x equivalent | 125.0 g |

$$x = \frac{125.0}{49.05} = 2.55$$

*Thus, normality of the solution is 2.55 N.*

4. What volume of distilled water and 30.0 m/V% hydrogen peroxide solution is needed to obtain 6.0 $dm^3$ of 1.5 m/V% hydrogen peroxide solution?

Solution of the problem needs application of the mixing equation:

$$\begin{array}{ll} c_1 = 30.0 \text{ m/V\%} & V_1 = x \\ \underline{c_0 = 1.5 \text{ m/V\%}} & \underline{V_0 = 6000.0 \text{ cm}^3} \end{array}$$

$$30.0 \cdot x = 6000.0 \cdot 1{,}5$$

$$x = \frac{6000.0 \cdot 1.5}{30.0} = 300.0 \text{ cm}^3$$

*Thus, 300. $cm^3$ 30 m/V% hydrogen peroxide solution and 5700.0 $cm^3$ distilled water is needed.*

5. Calculate the m/m% concentration of the solution that was prepared by dissolving additional 20.0 g of solute in 180.0 g of 10.0 m/m% solution?

180.0 g of 10.0 m/m% solution contains 18.0 g of solute and 162.0 g of solvent. After dissolving additional 20.0 g of solute, the total amount of solute is 38.0 g.

Thus,

$$\begin{array}{ll} 38.0 \text{ g of solute} & \text{in } 162.0 + 38.0 = 200.0 \text{ g of solution} \\ \underline{x \text{ g}} & \underline{\text{in } 100.0 \text{ g}} \end{array}$$

$$x = \frac{38.0 \cdot 100.0}{200.0} = 19.0 \text{ g}$$

*Thus, the m/m% concentration of the obtained solution is 19.0 m/m%.*

6. 5.0 g of sugar was dissolved in 73.0 g of water. Calculate the m/m% concentration the obtained solution.
7. Calculate normality and molarity of the 12.5 m/V% sulphuric acid solution. $M(H_2SO_4) = 98.1$ g/mol
8. Calculate the number of gram equivalents of $CaCl_2$ in 50.0 $cm^3$ of 0.07 mol/$dm^3$ calcium chloride solution. Calculate the g/$dm^3$ concentration of the solution. $M(CaCl_2) = 111.0$ g/mol
9. In 180.0 g of 10.0 m/m% solution additional 20.0 g of solute was dissolved. Calculate the m/m% concentration of the obtained solution.
10. 2.0 moles of sodium hydroxide are dissolved in 1500.0 g of water. Calculate molality, mole fraction, and the m/m% concentration of the obtained solution. M(NaOH) = 40.0 g/mol
11. How to prepare 150.0 $cm^3$ of 0.12 M sodium hydroxide solution? Calculate the m/V% of the solution? M(NaOH) = 40.0 g/mol
12. Calculate the m/V% concentration, molarity and normality of a solution of which 22.5 $cm^3$ volume contains 1.3 g $Ca(OH)_2$. $M(Ca(OH)_2) = 74.1$ g/mol
13. Calculate molarity and molality of a 5.1 m/m% sulphuric acid solution ($\rho$ = 1.032 g/$cm^3$). $M(H_2SO_4) = 98.1$ g/mol
14. How many times should a 160 g/$dm^3$ acetic acid solution be diluted to obtain a solution of 0.10 M final concentration? $M(CH_3COOH) = 60.1$ g/mol

15. What are the molarity and the molality of the 15.95 m/m% cane sugar solution? ($\rho$ = 1.063 g/cm$^3$). M($C_{12}H_{22}O_{11}$) = 342.3 g/mol
16. The m/m% concentration of a 2.46 mol/dm$^3$ ammonium sulphate solution is 28.0 m/m%. Calculate the density ($\rho$) and the Raoult concentration of the solution. M($(NH_4)_2SO_4$) = 132.1 g/mol
17. Calculate molarity, molality and the m/m% concentration of a phosphoric acid solution in which the mole fraction of phosphoric acid is 0.216. ($\rho$ = 1.426 g/cm$^3$). M ($H_3PO_4$) = 98.0 g/mol
18. What volume (cm$^3$) of water is needed to mix with 123.0 cm$^3$ of 5.00 m/V% $Na_2SO_4$ solution to obtain a 4.15 m/V% $Na_2SO_4$ solution?
19. In what a mass (g) of 4.0 m/m% $CuSO_4$ solution should 200.0 g of $CuSO_4 \cdot 5\,H_2O$ be dissolved to obtain a 16.0 m/m% $CuSO_4$ solution? M($CuSO_4$) = 159.6 g/mol, M($CuSO_4 \cdot 5\,H_2O$) = 249.7 g/mol
20. What volume (cm$^3$) of 60.0 m/m% phosphoric acid solution ($\rho$ = 1.426 g/cm$^3$) should be diluted to obtain 370.0 cm$^3$ of 2.5 M ortophosphoric acid solution? M ($H_3PO_4$) = 98.0 g/mol
21. 100.0 cm$^3$ of 24.0 m/m% $K_2CO_3$ solution ($\rho$ = 1.232 g/cm$^3$) is diluted with 50.0 g of distilled water. Calculate the Raoult concentration of the obtained solution. M($K_2CO_3$) = 138.2 g/mol
22. 2.0 dm$^3$ of 40.0 m/m% acetic acid solution ($\rho$ = 1.049 g/cm$^3$) and 3.0 dm$^3$ of 2.0 M acetic acid solution (d = is 1.015 g/cm$^3$) are mixed. Calculate the mole percent concentration of the obtained solution. M($CH_3COOH$) = 60.1 g/mol
23. What volume (cm$^3$) of 35.2 m/m% hydrochloric acid solution ($\rho$ = 1.17 g/cm$^3$) is needed to obtain 300.0 cm$^3$ of 26.2 m/m% hydrochloric acid solution (d = 1.13 g/cm$^3$)?
24. What volume (cm$^3$) of 30 m/m% sodium hydroxide solution ($\rho$ = 1.33 g/cm$^3$) is needed to prepare750.0 cm$^3$ of 2.0 mol/dm$^3$ sodium hydroxide solution? M(NaOH) = 40.0 g/mol
25. What is the pH of the solution that is obtained by mixing of 200.0 g of 4.9 m/m% of sulphuric acid solution and 200.0 g of 10.0 m/m% sodium hydroxide solution? What amount of unreacted reagent can be found in the obtained solution? M($H_2SO_4$) = 98.1 g/mol, M(NaOH) = 40.0 g/mol

# VI Reaction kinetics

The aim of reaction kinetics is to determine dependence of rate of reactions on the physical state and chemical composition of the system and what molecular events occur during the overall reactions. A *system* is a macroscopic region of the universe, defined by boundaries or walls of particular natures, together with the physical surroundings of that region, which determine processes that are allowed to affect the interior of the region. All space in the universe outside the thermodynamic system is known as the *surroundings*, the *environment*.

The systems within the chemical reactions occur can be classified according to several aspects. The system can be composed of one phase (*homogeneous system*) or two or more phases (*heterogeneous system*). According to this classification we can distinguish homogeneous reactions which take place in single phase and heterogeneous reactions, in which the reactants are components of two or more phases or in which one or more reactants undergo chemical change at an interface.

A system is separated from its surroundings by a *boundary*, which may be notional or real but, by convention, delimits a finite volume. Transfers of work, heat, or matter and energy between the system and the surroundings may take place across this boundary. A thermodynamic system is classified by the nature of the transfers that are allowed to occur across its boundary, or parts of its boundary.

An *isolated system* is an idealized system that has no interaction with its surrounding. Mass and energy remains constant within the system, and no energy or mass transfer takes place across the boundary. In a *closed system*, no mass may be transferred in or out of the system boundaries. The system always contains the same amount of matter, but heat and work can be exchanged across the boundary of the system. In an *open system*, matter may flow in and out of some segments of the system boundaries. There may be other segments of the system boundaries that pass heat or work but not matter.

Rate of chemical reactions occurring in a homogeneous phase affected by the following factors:

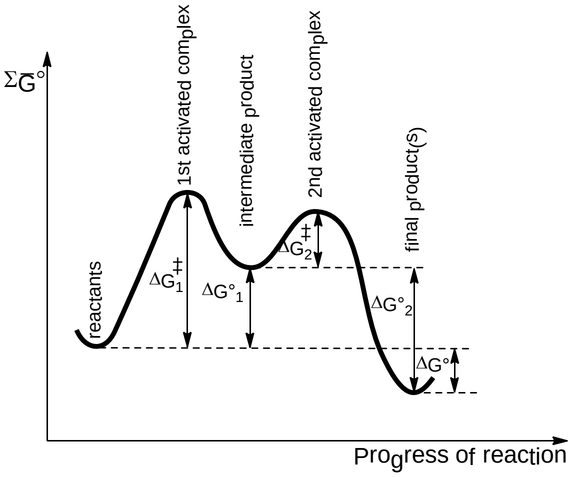
- nature of reagents
- state of matter
- concentration of reactants
- temperature of the system
- concentration of catalyst (if any)
- pressure (in case of gas phase reactions)

### Reaction mechanism

In most of the cases mechanism of reactions specified by stoichiometric equations is more complex than it is represented by the gross stoichiometric equation. The reaction may take place in several steps. An *elementary reaction* is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step. An elementary reaction can be explained by the *transition state theory* of reactions. According to this theory a reaction is resulted from collision of two molecules (reactant particles) forming an unstable group of atoms (activated complex) that can break up to form the products (Figure VI-1).

A set of elementary reactions comprises *a reaction mechanism*, which predicts the elementary steps involved in a *complex reaction*. Complex reactions are combination of consecutive or parallel elementary reactions. Reaction profile of a complex reaction is shown in Figure VI-1.

**Figure VI-1:** Reaction profile of a complex reaction



Elementary reactions are classified according to their *molecularity*. Molecularity is the number of molecules (ions, radicals) on the reactant side of an elementary reaction. A *unimolecular* reaction is an elementary reaction that involves one reactant molecule (e.g., spontaneous decomposition reactions). A *bimolecular* reaction is an elementary reaction that involves two reactant molecules. Bimolecular reactions are the most common. Some gas-phase reactions are thought to occur in a *termolecular* reaction, an elementary reaction that involves three reactant molecules.

### Reaction rate

The rate of a reaction is the amount of product formed or the amount of reactant used up per unit of time. In other words, the reaction rate is the increase in molar concentration of product of a reaction per unit time, or the decrease in molar concentration of reactant per unit time. Considering the generalized reaction

$$A + B \rightarrow C$$

the reaction rate is given by the following expressions:

$$v = \frac{-\Delta[A]}{\Delta t} \quad ; \qquad v = \frac{-\Delta[B]}{\Delta t} \quad ; \qquad v = \frac{\Delta[C]}{\Delta t}$$

where e.g. $\Delta[A]$ is the decrease of molar concentration of reactant „$A$” in the time interval $\Delta t$ . (Note: The rate of a reaction is always positive. A negative sign is present to indicate the reactant concentration is decreasing.)

The reaction rate is well defined if the change in concentration (*d*C) is related to a short (*d*t) time interval (it is expressed by fractional differential equation)

$$v = \pm \frac{dC}{dt}$$

To obtain the reaction rate, concentration of a reactant or a product should be determined during the course of the reaction. Based on analysis of graphical representation of the corresponding concentration-time data, the mathematical function describing the relation between the two sets of data (*rate equation* or *rate law*) can be determined.

There have been developed several different methods for determination of the rate equation. The most common way to determine the rate equation for a particular reaction, the reaction rate with a mass balance for the system is combined. For a generic reaction $aA + bB \rightarrow cC$ with no intermediate steps in its reaction mechanism (that is, an elementary reaction), the rate is given by the generalized equation

$$v = k[A]^{\alpha}\,[B]^{\beta}$$

where

$v$ = rate of the reaction,
$k$ = rate coefficient or rate constant,
[A] = concentration of reactant „A" (mol/dm$^3$)
[B] = concentration of reactant „B" (mol/dm$^3$)
$\alpha$ = partial order of the reaction with respect to reactant „A" and
$\beta$ = partial order of the reaction with respect to reactant „B"
$\alpha+\beta$ = overall order of the reaction

The exponent $\alpha$ and $\beta$ are frequently, but not always, integers. They must be determined experimentally and cannot be obtained simply by looking at the balanced equation. Elementary (single-step) reactions do have reaction orders equal to the stoichiometric coefficients for each reactant. Complex (multi-step) reactions may or may not have reaction orders equal to their stoichiometric coefficients. The *rate constant* is proportionality constant in the relationship between rate and concentrations. Its value depends on conditions such as temperature, ionic strength, and surface area of the adsorbent.

The rate equation is a differential equation, which can be integrated to obtain *an integrated rate equation* that links concentrations of reactants or products with time.

## First order reactions

If a reaction rate depends on a single reactant and the value of the exponent is 1, then the reaction is said to be first order.

$$v = k[A]$$

The rate of the reaction ($v$) can be expressed as a decrease of the concentration of the reactant as a function of time:

$$-\frac{d[A]}{dt} = k[A]$$

Solution of the differential equation gives the rate constant ($k$):

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

where

$[A]_0$ = initial concentration of reactant „A" (t=0 ); and
$[A]_t$ = concentration of reactant „A" at the timepont „t".

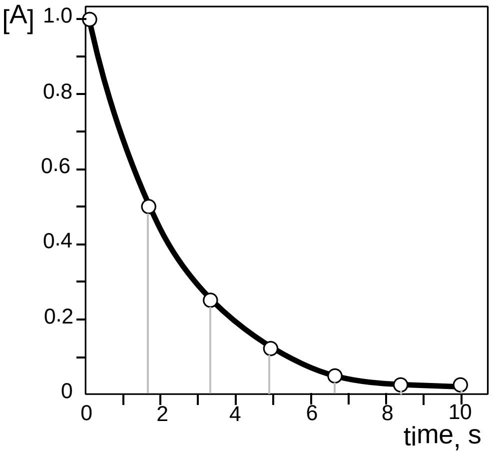
The order of the reaction can be determined by determination of half-life ($t_{1/2}$) of the reaction. Half-life of a reaction is the time it takes for the reactant concentration to decrease to one-half of its initial concentration $[A]_{t\,(½)} = [A]_{0/2}$. Then

$$t_{\left(\frac{1}{2}\right)} = \frac{2.303}{k}\log\frac{[A]_0}{[A]_{0/2}}$$

$$t_{\left(\frac{1}{2}\right)} = \frac{2.303}{k}\log 2 = \frac{0.693}{k}$$

As it is shown (Figure VI-2.) half-life of a first order reaction is independent of initial concentration of the reactant. The half-life of the reaction can be used to determine rate constant of the reaction.

**Figure VI-2:** Concentration-time plot of a first order reaction



## Second order reactions

If a reaction rate depends on the second power of concentration of a single reactant or the concentration of two reactants, then the reaction is said to be second order

$$v = k[A]^2\text{, or}$$

$$v = k[A][B]$$

Analysis of the concentration-time data can be simplified if the initial concentrations of the two reactants are equal. Under such conditions

$$k = \frac{1}{t}\cdot\left(\frac{[A]_t}{[A]_0([A]_0 - [A]_t)}\right)$$

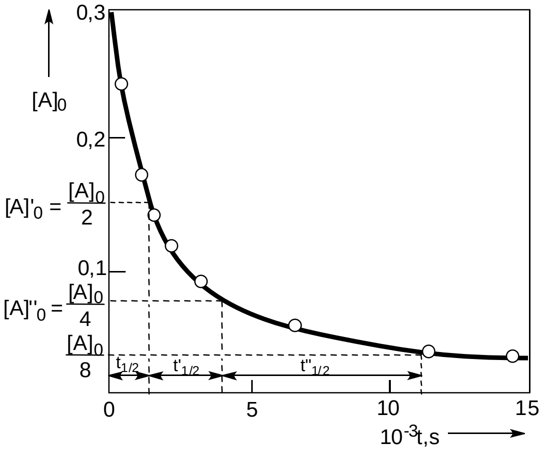
where

$[A]_0$ = initial concentration of reactants „A” and „B” (t=0); and
$[A]_t$ = concentration of reactants „A” and „B” at the time Pont „t”.

The half-life of second order reactions is inversely proportional to the second power of the initial concentration (the higher the initial concentration the shorter the half-life; Figure VI-3):

$$t_{1/2} = \frac{1}{k}[A]_0$$

**Figure VI-3:** Concentration-time plot of a second order reaction



A second order reaction has a rate equation that involves two reactants,”A” and “B”. If one of the reactants, “A”, for example, would have a significantly high concentration, while the other reactant, “B”, would have a significantly low concentration., it can be assumed that concentration of reactant “A” remains constant during the reaction, because its consumption is so small that the change in concentration becomes negligible. As a result, the reaction will become a kinetically firs order (*pseudo first order*) reactions.

## Zeroth order reactions

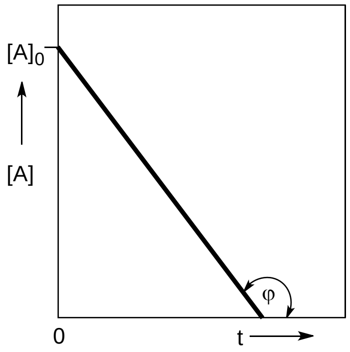
A *zeroth order reaction* is a reaction that proceeds at a rate that is independent of reactant concentration (Figure VI-4). This means that rate of the reaction is equal to the rate constant, *k*.

$$v = k\,[A]^0 = k$$

The half-life of the reaction is directly proportional to the initial concentration of the reactant:

$$t_{1/2} = \frac{[A]_0}{2k}$$

**Figure VI-4:** Concentration-time plot of a zeroth order reaction



There are two general conditions that can give rise to zero-order rates:

1. Only a small fraction of the reactant molecules are in a location or state in which they are able to react, and this fraction is continually replenished from the larger pool.
2. When two or more reactants are involved, the concentrations of some are much greater than those of others

## Temperature dependence of reaction rate

Usually, an increase in temperature is accompanied by an increase in the reaction rate. The mathematical equation which expresses dependence of the rate constant on temperature is called the *Arrhenius equation*

$$k = A \cdot \exp\left(-\frac{E}{RT}\right)$$

where

$k$ = rate constant;
$A$ = pre-exponential factor;
$E$ = activation energy
$R$ = universal gas constant
$T$ = thermodynamic temperature

The relationship is only valid when heat is the only form of the activation energy of the reaction. A general rule of thumb for most (not all) chemical reactions is that the rate at which the reaction proceeds will approximately double for each 10 °C increase in temperature.

The *Arrhenius equation* is purely empirical. The effect of temperature on the rate of reactions can be explained on the basis of the collision and the transition state theories.

## Catalysis

Catalysis is the increase in rate of a reaction as the result of addition of a *catalyst*. Catalysts are involved in the reaction; they are taking place in formation of the activated complexes, and regenerated to their original form in the end of the reaction. Catalysed reactions have lower *activation energy* than the corresponding uncatalysed reaction, resulting in a higher reaction rate at the same temperature.

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The opposite of a catalyst, a substance that reduces the rate of a reaction, is an *inhibitor*. Chemical species that improve catalytic activity of a catalyst are called *co-catalysts* (or *promoters).*

## VI.1 **Demonstration:** Landolt experiment

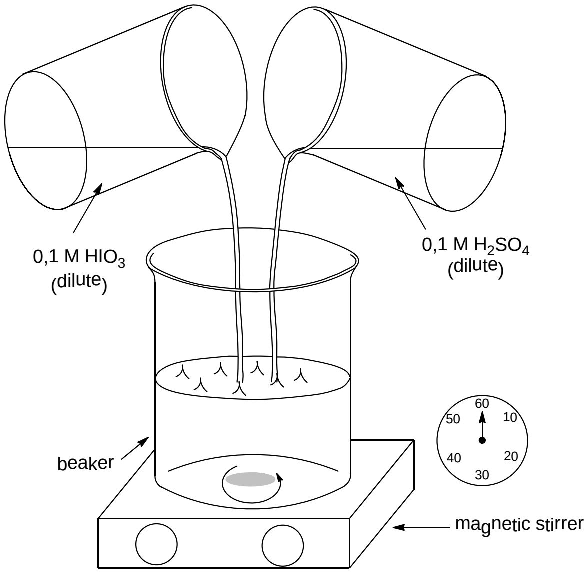
Reaction of iodic acid with sulphurous acid comprises three consecutive steps:

$HIO_3 + 3\,H_2SO_3 = HI + 3\,H_2SO_4$ (slow)
$5\,HI + HIO_3 = 3\,I_2 + 3\,H_2O$ (fast)
$I_2 + H_2SO_3 + H_2O = 2\,HI + H_2SO_4$ (fast)

Iodic acid is applied in excess and for the easy detection of traces of iodine starch solution is added. Hydrogen iodide formed slowly in the initial reaction step is oxidized by iodic acid to elementary iodine in the second fast step. It is expected that after mixing the reactants an immediate blue coloration would occur (the colour of iodine-starch complex). Instead, for a longer period of time no change in colour can be observed due to the third, very fast reaction which consumes iodine. Thus, the actual concentration of iodine is being maintained undetectable until the total amount of the scavenger (sulphurous acid) vanishes. Then, the excess of iodic acid may produce iodine in a detectable amount, according to the second equation and the reaction mixture turns blue. Thus the time for complete disappearance of sulphurous acid is measured. The shorter the time elapsed till blue coloration (reaction time), the faster the reaction.

The apparatus is shown in Figure VI-4. The magnetically stirred reaction mixtures are set to perform the series in constant volumes for an easier comparison. The stopwatch is started when the stock solutions are poured in, and stopped when the blue colour of iodine-starch appears. The table below is filled in according to the reaction conditions and the results are discussed.

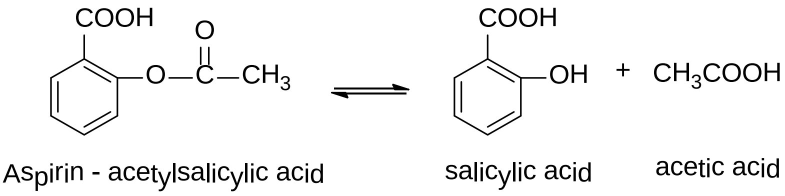
**Figure VI-5:** The Landolt experiment



| Temperature (°C) | $HIO_3$solution ($cm^3$) | $H_2SO_3$ solution ($cm^3$) | Distilled water + starch solution ($cm^3$) | Reaction time (s) |
|---|---|---|---|---|
| | 20 | 20 | 400 | |
| | 20 | 20 | 400 | |
| | 20 | 20 | 400 | |
| | 20 | 20 | 400 | |
| | 30 | 20 | 390 | |
| | 40 | 20 | 380 | |
| | 50 | 20 | 370 | |

## VI.2 Experimental task: Investigation of temperature- and pH-dependence of the rate of hydrolysis of acetylsalicylic acid (ASA)

Hydrolysis of the drug entity can be a major factor in the instability of solutions. Aspirin (acetylsalicylic acid**)** for example, undergoes hydrolysis with the resultant degradation products being salicylic acid and acetic acid.



The rate of this reaction is said to be second order, since it is dependent not only upon the aspirin concentration, but upon the hydronium ion concentration in solutions with pH values less than approximately 2.5, or upon the hydroxyl ion concentration in solution with pH values greater than approximately 7.0. If the solution is buffered so that the hydroxyl ion concentration remains essentially constant, the rate of hydrolysis follows first order kinetics.

### 1. Investigation of temperature-dependence of rate of hydrolysis

Accurately weighed 120 mg of acetylsalicylic acid is dissolved in distilled water in a 100 $cm^3$ volumetric flask. About a 25 $cm^3$ aliquot of the solution - in a dark, closed bottle - are kept in a water bath thermostatically controlled at a temperature of 60 ±1 °C, for 60 minutes. A similar experiment is performed in a water bath controlled at a temperature of 80 ±1 °C.

During incubation 5.00 $cm^3$ samples are taken at the 20, 40 and 60 minute time points and the samples are immediately diluted with 5.00 $cm^3$ of distilled water. To 1.00 $cm^3$ of the diluted solution 4.00 $cm^3$ of 1% iron(III) chloride solution is added, and the sample is kept in the dark for 15 minutes. Then, the absorbance of the solution is measured at 530 nm using a spectrophotometer against the mixture of 1.00 $cm^3$ water and 4.00 $cm^3$ of iron(III) solution (blank).

2. **Investigation of pH- dependence of rate of hydrolysis**

Accurately weighed 120 mg of acetylsalicylic acid is dissolved in sodium carbonate ($Na_2CO_3$) solution of known concentration in a 100 $cm^3$ volumetric flask. The concentration of the sodium carbonate solutions are

I. 0.00625 M $Na_2CO_3$
II. 0.0125 M $Na_2CO_3$
III.0.025 M $Na_2CO_3$

After dissolution, the pH of the acetylsalicylic acid solutions is determined by potentiometric measurements.

About a 25 $cm^3$ aliquot of each solution - in a dark, closed bottle - is kept in a water bath thermostatically controlled at a temperature of 60 ±1 °C, for 60 minutes.

At the end of incubation 5.00 $cm^3$ sample is taken and immediately diluted with 5.00 $cm^3$ of distilled water. To 1.00 $cm^3$ of the diluted solution 4.00 $cm^3$ of 1% iron(III) chloride solution is added and the sample is kept in the dark for 15 minutes. Then, the absorbance of the solution is measured at 530 nm using a spectrophotometer against the mixture of 1.00 $cm^3$ water and 4.00 $cm^3$ of iron(III) solution (blank).

Salicylic acid concentration of the measured solution can be calculated by means of the calibration graph provided by the practice leader.

Based on the results of the first set of experiments, calculate the *pseudo first order rate constant* (*k*') for both temperatures, the value of the activation energy, as well as the rate constant and the half-life of the reaction at room temperature (20 °C).

Based on the results of the second set of experiments calculate the *pseudo first order rate constant*s of the hydrolysis occurring in the solutions of different pH. (MW(acetylsalicylic acid) = 180, MW(salicylic acid) = 138.12)

## VI.3 Calculations

1. Decomposition of $N_2O_5$ occurs according to the following rate equation:

$$-\frac{d\left[N_2O_5\right]}{dt} = k\cdot\left[N_2O_5\right] = 3\cdot 10^{-2}\ \min^{-1}$$

What is the half-life of the reaction?

According to the integrated rate equation of the first order reactions:

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{3.00\cdot 10^{-2}} = 23.1\ \text{minutes}$$

*Thus, the half-life of the reaction is 23.1 minutes.*

2. Ethyl acetate undergoes base-catalysed hydrolysis according to the following stoichiometry:

$$CH_3COOC_2H_5 + OH^- = CH_3COO^- + C_2H_5OH$$

The second order rate constant of the reaction is 5.45 $dm^3 mol^{-1} min^{-1}$ at 20 °C. Calculate the concentration of ethyl acetate at the 20 minute reaction time if 1 $dm^3$ of 0.0400 M ethyl acetate solution was mixed with 1 $dm^3$ of 0.0400 M potassium hydroxide solution. Temperature of both solutions was 20 °C.

On mixing concentration of both reactants is halved. Thus,

$$[CH_3COOC_2H_5]_0 = 0.020 \text{ M}$$

$$[KOH]_0 = 0.020 \text{ M}$$

The ethyl acetate concentration at the 20 minute reaction time:

$$\frac{1}{[EtOAc]_{20}} = \frac{1}{[EtOAc]_0} + k \cdot t$$

$$\frac{1}{[EtOAc]_{20}} = \frac{1}{0.020} + 5.45 \cdot 20$$

$$\frac{1}{[EtOAc]_{20}} = 50 + 109 = 159$$

$$[EtOAc]_{20} = 6.29 \cdot 10^{-3} \text{ M}$$

*Thus, the concentration of ethyl acetate at the 20. minute time point is* $6.3 \cdot 10^{-3}$ *M.*

3. A 0.150 M ammonium cyanate undergoes isomerization into urea:

$$NH_4OCN \quad = \quad NH_2(CO)NH_2$$

The reaction follows second order kinetics. The first half-life of the reaction is 9 hours and 27 minutes. What a mass of urea is formed in 1 $dm^3$ reaction mixture at the 10 hours' time point? $M(NH_2(CO)NH_2) = 60.06$ g/mole

For second ordered reactions:

$$t_{1/2} = \frac{1}{k \cdot [A]_0}$$

9 hours and 27 minutes = 567 minutes

$$567 = \frac{1}{k \cdot 0.150}$$

$$k = \frac{1}{567 \cdot 0.150}$$

$$k = \frac{1}{85.05} = 0.012\ \mathrm{dm^3 mol^{-1} min^{-1}}$$

10 hours= 600 minutes

Based on solution of the previous calculation problem:

$$\frac{1}{[NH_4OCN]_{600}} = \frac{1}{0.150} + 0.012 \cdot 600$$

$$\frac{1}{[NH_4OCN]_{600}} = 6.67 + 7.20 = 13.87$$

$$[NH_4OCN]_{600} = \frac{1}{13.87} = 0.072\ \mathrm{mol}$$

Thus, the amount of isomerized ammonium cyanate (equal to the amount of urea) in the 1 dm$^3$ of reaction mixture is:

0.150 – 0.072 = 0.078 mol.

| | |
|---|---|
| 1 mol urea | 60.06 g |
| 0.078 mol urea | x g |

x = 0.078 · 60.06 = 4.7 g

*Thus, it is 4.7 g urea formed in the reaction mixture over the 10 hours reaction time.*

4. The counts of a sample from Sneferu pharaoh’s tomb containing 1.0 g amount of carbon is 8.1 per minute. Calculate the age of the sample if the count of a living organism containing 1.0 g amount of carbon is 15.3 per minute. ($t_{1/2}$ ($^{14}$C) = 5760 years).

For a given element, the decay or disintegration rate is proportional to the number of atoms and the activity (counts) measured in terms of atoms per unit time. The counts ($A$) measured in the 1.0 g amount of organic ($^{14}$C-containg) sample is directly proportional to the number of the $^{14}$C isotopes (N): $A = k \cdot N$.

Since the decay rate is dependent upon the number of radioactive atoms, in terms of chemical kinetics, one can say that radioactive decay is a *first order reaction process*. The decay can be characterized by *half-life* of the process. Half-life is the time period that is characterized by the time it takes for half of the substance to decay:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

where

*k = decay constant*

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5760} = 1.20 \cdot 10^{-4}\ year^{-1}$$

*Thus, the decay constant of the disintegration is 1.20 · 10 $^{4}$ years.*

According to the relationship describing first order kinetics:

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - k \cdot t$$

$$8.1 = 15.3 - 1.20 \cdot 10^{-4} \cdot t$$

$$t = \frac{15.3 - 8.1}{1.20 \cdot 10^{-4}} = \frac{7.2}{1.20 \cdot 10^{-4}} = 6.0 \cdot 10^{4} \text{ years}$$

*Thus, the age of the sample is 6.0 · 10$^{4}$ years.*

5. Radioactivity of a substance is reduced to ¼ of its initial activity in 25.0 s. What is the first order reaction rate constant of the radioactive decay?

For first order reactions:

$$k = \frac{2.303}{t} \cdot \log \frac{[A]_0}{[A]_t}$$

Thus,

$$k = \frac{2.303}{25} \cdot \log \frac{1}{1/4}$$

$$k = 0.092 \cdot \log 4 = 0.092 \cdot 0.602 = 0.055 = 5.5\ 10^{-2}\ \mathrm{s}^{-1}$$

*Thus, the first order reaction rate constant of the radioactive decay is 5.5 · 10$^{-2}$ s$^{-1}$.*

# VII Chemical equilibrium

## VII.1 Law of mass action

Many chemical reactions do not run to completion. After they are started, they appear to slow down and finally stop without converting the total amount of stating materials to products. Reaction of acetic acid with ethyl alcohol to form ethyl acetate and water is one of such reactions.

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Such reactions are *reversible* and form a mixture of reactants and products in a *dynamic equilibrium*. This dynamic equilibrium consist of a forward reaction, in which substances react to give products and a reverse reaction , in which products react to give the original reaction.

Equilibrium reactions can be described in general as follows:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

The equilibrium mixture is composed of two reactions:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \qquad \text{(forward reaction)}$$

$$c\,C + d\,D \rightleftharpoons a\,A + b\,B \qquad \text{(backward reaction)}$$

The rate of the forward reaction ($v_f$) continuously decreases due to the decrease of concentration of reactants A and B, while the rate of the backward reaction ($v_b$) continuously increases due to the increase of concentration of products C and D, until eventually they become equal. When this happens, the concentration of the reactants and the products no longer changes, as the reaction mixture has reached its equilibrium. The *chemical equilibrium* is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal.

The composition of the equilibrium mixture can be characterized by the numerical value of the equilibrium constant expression. The *equilibrium-constant expression* for a reaction is an expression obtained by multiplying the concentrations of products, dividing their product by the product of concentrations of reactants, while raising each concentration term to a power equal to the coefficient in the chemical equation.

$$K_c = \frac{[C]^c \,.\, [D]^d}{[A]^a \,.\, [B]^b}$$

where the values indicated in brackets are the mol/dm$^3$ concentrations (equilibrium concentrations) of the compounds in the equilibrium mixture, while *a*, *b*, *c* and *d* are the respective stoichiometric coefficients.

The numerical value of equilibrium constant expression can be determined experimentally at a given temperature. The *equilibrium constant* ($K_c$) is the value obtained for the equilibrium constant expression when equilibrium concentrations are substituted. The equilibrium constant is a characteristic physico-chemical data of the system at a given temperature. The *law of mass action* is a relation that states that the numerical value of the equilibrium-constant expression, $K_c$ is constant for a particular reaction at a given temperature, whatever equilibrium concentrations are substituted.

## VII.2 The Le Chatelier principle

When a system is in chemical equilibrium, there is no detectable change in its composition as long as the reaction conditions are unchanged. A useful qualitative statement about the influence that the change of conditions can produce on the composition of equilibriums is attributed to the French chemist *Le Chatelier* (1884). Le Chatalier's principle states, if a system in a chemical equilibrium is altered by the change of some condition, chemical reaction occurs to shift the equilibrium composition in a way that acts to reduce the effect of that change of condition. The applicability of this principle is shown by the following examples:

a. *Changing concentrations*. When more reactant is added to, or some product is removed from, an equilibrium mixture, thereby changing the concentration of reactant or product, net reaction occurs left to right (that is, in the forward direction) to give a new equilibrium, and more products are produced When more product is added to, or some reactant is removed from, an equilibrium mixture, thereby changing the concentration of reactant or product, net reaction occurs right to left (that is, in the reverse direction) to give a new equilibrium, and more reactants are produced.
b. *Changing the temperature.* Temperature has a profound effect on most reactions. In the first place, reaction rates usually increase with an increase in temperature, meaning that equilibrium is reached sooner. Second, *equilibrium constants vary with temperature*. For an *endothermic reaction* ($\Delta H$ positive), the amounts of products are increased at equilibrium by an increase in temperature ($K$ is larger at higher T). For an *exothermic reaction* ($\Delta H$ negative), the amounts of products are increased at equilibrium by a decrease in temperature ($K$ is larger at lower T).
c. *Changing the partial pressure of a gaseous reactant.* A pressure change *obtained by changing the volume of the equilibrium mixture* can affect the equilibrium composition of a gas phase reaction. If the pressure is increased *by decreasing the volume of a reaction mixture*, the reaction shifts in the direction of formation of fewer moles of gas. On the other hand, if the pressure is decreased *by increasing the volume of a reaction mixture,* the reaction shifts in the direction of formation of more moles of gas. The system seeks keeping its initial pressure.

## VII.3 Equilibriums in electrolytes

When dissolving, some groups of compounds are dissociating partly or completely into hydrated ions. This process is referred to as *electrolytic dissociation* and the dissociating compounds are called *electrolyte*s. Based on their chemical nature electrolytes can be divided into three main groups: *acids*, *bases* and *salts*.

### VII.3.1 Acids and bases

### VII.3.1.1 Acid-base theory of Arrhenius

Definition of acids and bases has been altered several times. One of the first classifications of acids and bases was made by *Arrhenius* (1888). In *Arrhenius's* definitions, an *acid* is any substance that, when dissolved in water, increases the concentration of hydrogen (hydronium) ions, while a *base* is any substance that, when dissolved in water, increase the concentration of the hydroxide ions.

Aqueous solutions of acids have acidic properties, because the hydrogen (hydronium) ion concentration is higher than that of the hydroxide ions. For example, hydrochloric acid ($HCl_{(aq)}$), sulphuric acid ($H_2SO_{4(aq)}$), nitric acid ($HNO_{3(aq)}$), etc.

Bases dissociate to hydroxide ions in their aqueous solutions. In aqueous solutions of bases concentration of the hydroxide ions exceeds that of the hydrogen ions. For example, sodium hydroxide ($NaOH_{(aq)}$, potassium hydroxide ($KOH_{(aq)}$), calcium hydroxide ($Ca(OH)_{2(aq)}$), etc.

Acids and bases react with each other in *neutralization* reactions. For example:

$$HCl_{(aq)} + NaOH_{(aq)} = NaCl_{(aq)} + H_2O_{(l)}$$

$$HNO_{3(aq)} + KOH_{(aq)} = KNO_{3(aq)} + H_2O_{(l)}$$

### VII.3.1.2 Acid-base theory of Brønsted and Lowry

*J. N. Brønsted* and *T. M. Lowry* extended the acid-base theory of *Arrhenius* and emphasized the role of hydrogen ion (proton) in the acid-base reactions. According to the Brønsted and Lowry theory, an *acid*s is a species that donates a proton to another species in a proton-transfer reaction. They defined a *base* as a species that accepts a proton in a proton-transfer reaction.

According to their theory, acids are converted into a base by releasing a proton and a base is transformed to an acid by accepting a proton. (See examples below.) An acid donates a proton only in the presence of a proton acceptor base. Accordingly, conversion of an acid to the respective base and conversion of a base to its respective acid takes place in the same reaction.

Examples:

| **$Acid_1$** | | **$Base_2$** | | **$Base_1$** | | **$Acid_2$** |
|---|---|---|---|---|---|---|
| HCl | + | $H_2O$ | = | Cl- | + | $H_3O^+$ |
| $NH_4^+$ | + | $H_2O$ | = | $NH_3$ | + | $H_3O^+$ |
| $H_3O^+$ | + | $OH^-$ | = | $H_2O$ | + | $H_2O$ |
| $H_2O$ | + | $NH_3$ | = | $OH^-$ | + | $NH_4^+$ |

The corresponding acid-base pairs (e.g. HCl and $Cl^-$, $NH_4^+$ and $NH_3$, etc.) are conjugate acid-base pairs. A *conjugate acid-base pair* consists of two species in an acid-base equilibrium, one acid and one base, which differ by gain or loss of a proton.

Some compounds (for example $H_2O$ and $NH_3$ molecules, $HCO_3^-$ and $H_2PO_4^-$ ions, etc.) can act either as an acid or a base depending on the relative acid-base strength of the reaction partner. These species are *amphiprotic* (amphoteric) species.

### VII.3.1.3 Acid-base theory of Lewis

*G. N. Lewis* realized that the concept of acids and bases can be generalized to include reactions (e.g. reaction of acidic and basic oxides) that do not fit either the *Arrhenius* or the *Brønsted-Lowry* concepts.

According to this theory, *a Lewis acid* is a species (atom, molecule, or ion) that can form a covalent bond by accepting a pair of electrons from another species, while a

*Lewis base* is a species (atom, molecule, or ion) that can form a covalent bond by donating an electron pair to another species.

The compounds that are classified as acids or bases according to the *Arrhenius* or the *Brønsted-Lowry* theory can also be considered as acids or bases according to the *Lewis concept*. According to the Lewis concept, however, the group of the compounds considered to be acids or bases further extends and numerous chemical reactions can be interpreted as acid-base reactions.

Examples:

| **Lewis acid** | | **Lewis base** | | **Lewis acid-base complex** |
|---|---|---|---|---|
| $BF_3$ | + | $NH_3$ | = | $F_3BNH_3$ |
| $AlCl_3$ | + | $Cl^-$ | = | $AlCl_4^-$ |
| $Fe^{2+}$ | + | $6\ H_2O$ | = | $[Fe(H_2O)_6]^{2+}$ |
| $SO_3$ | + | $BaO$ | = | $BaSO_4$ |
| $Ag^+$ | + | $2\ NH_3$ | = | $[Ag(NH_3)_2]^+$ |

### VII.3.1.4 Self-ionisation of water, the pH

According to the *Brønsted-Lowry* theory water is an amphoteric compound: it can react either as an acid or a base. Because of this dual acid-base character, water molecules can react with each other in an acid-base reaction. The reaction is a reversible equilibrium process (see VII.3.1.2), in which a proton from one $H_2O$ molecule is transferred to another $H_2O$ molecule, leaving behind a hydroxide ion and forming a hydronium ion:

$$H_2O + H_2O \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

According to the law of mass action, the equilibrium constant expression can be obtained by multiplying the concentrations of products by each other, dividing their product by the product of concentrations of reactants, rising each concentration term to a power equal to the coefficient in the chemical equation:

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The numerical value of the above equilibrium constant expression is the equilibrium constant of dissociation of water. Since in pure water the extent of the above reaction is very low, the concentration of the non-dissociated water molecules (55.5 M) remains essentially constant. Thus, the above expression for the equilibrium constant can be written in a simpler form.

Rearranging the expression, moving $[H_2O]^2$ next to $K_d$, the ion product equals a constant:

$$K_c\ [H_2O]^2 = [H_3O^+][OH^-]$$

and thus:

$$K_w = [H_3O^+][OH^-]$$

The equilibrium value of the ion product $[H_3O^+][OH^-]$ is the *ion product constant for water*, indicated as $K_w$.

According to the law of mass action, in pure water and in aqueous solutions the product of mol/dm$^3$ concentration of the hydrogen ions (hydronium ions) and the hydroxide ions is constant. The value of the ion product constant of water at 25 °C and on a pressure of 0.1 MPa is $1.0 \cdot 10^{-14}$ mol$^2$/dm$^6$. Because of the stoichiometry of the above reactions of the water, in the pure water: $[H_3O^+] = [OH^-] = 1.0 \cdot 10^{-7}$ M.

Because the concentrations of the hydrogen ions and the hydroxide ions in aqueous solutions are rather low, the negative of the logarithm of their molar concentrations are used for their quantitative description. According to *S. P. L. Sørensen*, the pH is defined as the negative logarithm of the mol/dm$^3$ concentration of the hydronium ions. Accordingly,

$$pH = -\log [H_3O^+]$$

Similarly, we can define pOH as

$$pOH = -\log [OH^-]$$

Based on the above explanation, in pure water at 25 $^{o}$C pH = pOH = 7. The values under pH 7 (pH 0-7) are *acidic*, while the values above pH 7 (pH 7-14) characterise the *basic* solutions.

### VII.3.1.5 Equilibrium of the acidic dissociation, the pK$_a$

As it was stated previously, protolysis (electrolytic dissociation) of acids and bases is a reversible, equilibrium process. An acid reacts with water to produce hydronium ion (hydrogen ion) and its conjugate base ion. The process is called *acid ionization* or *acid dissociation*. The acid ionization equilibrium of a HA weak acid in aqueous solution is

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

For a strong acid, which completely ionizes in solution, concentrations of the formed ions can be calculated based on stoichiometry of the reaction and the initial concentration of the acid. For a weak acid such as acetic acid, however, the concentrations of ions in solution are determined by the *acid ionization (dissociation) constant*, which is the equilibrium constant for the ionization of the weak acid.

Applying the law of mass action for the above equilibrium:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

where $K_c$ = *equilibrium constant*.

Assuming that this is a dilute solution and that the reaction occurs to only a small extent, concentration of water will be nearly constant. Rearranging the equation results

$$K_a = K_c[H_2O] = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

where $K_a$ = *acid ionization (dissociation) constant*.

The $pK_a$ can be defined similar to the pH:

$$pK_a = -\log K_a$$

The higher the $K_a$ or the lower the $pK_a$ the stronger the acid against water.

### VII.3.1.6 Equilibrium of the basic dissociation, the $pK_b$

Equilibria involving weak bases (B) are treated similarly to those of weak acids. A base reacts with water to produce hydroxide ion and its conjugate acid ion. The process is called base ionization or base dissociation. The *base ionization equilibrium* of a B weak base in aqueous solution is

$$B_{(aq)} + H_2O = HB^+_{(aq)} + OH^-_{(aq)}$$

The corresponding *equilibrium constant* is

$$K_c = \frac{\left[HB^+\right]\left[OH^-\right]}{\left[B\right]\left[H_2O\right]}$$

Because the concentration of water is nearly constant, the equation can be rearranged as it was done for acid ionization:

$$K_b = K_c[H_2O] = \frac{\left[HB^+\right]\left[OH^-\right]}{\left[B\right]}$$

where $K_b$ is *the base ionization (dissociation) constant*.

The $pK_b$ can be defined similar to the $pK_a$:

$$pK_b = -\log K_b$$

The higher the $K_b$ or the lower the $pK_b$, the stronger the base against to water.

### VII.3.2 Salts

Salts are often prepared by neutralisation reaction of acids and bases. For example,

$$NaOH + HCl = NaCl + H_2O$$

$$KOH + H_2SO_4 = KHSO_4 + H_2O$$

The salts (with a few exceptions) are crystalline compounds forming ionic lattice and conduct electricity in their solutions and in molten state. Salts can be classified as:

1. *Regular salts*: $NaCl$, $K_2SO_4$, $NaNO_3$
2. *Acidic salts*: $KHSO_4$, $NaH_2PO_4$, $Na_2HPO_4$
3. *Basic salts*: $Bi(OH)_2NO_3$,
4. *Double salts*: $KAl(SO_4)_2$
5. *Complex salts*: $[Ag(NH_2)_2]Cl$, $K_3[Fe(CN)_6]$

A large number of salts form ionic lattice and release hydrated cations and hydrated anions when dissolved in water:

$$Me_mX_{n(s)} \;=\; m\,Me^{n+}{}_{(aq)} \;+\; n\,X^{m-}{}_{(aq)}$$

Such ions can react with the amphoteric water in an acid-base reaction producing hydronium or hydroxide ions, so they may give acidic or basic solutions. This process is *hydrolysis*. Based on the nature of ions take part in hydrolysis *anionic*, *cationic*, and *anionic-cationic hydrolysis* can be differentiated.

$$Me^{n+}{}_{(aq)} \;+\; n\,H_2O \;=\; Me(OH)_n \;+\; n\,H^{+}{}_{(aq)}$$

$$X^{m-}{}_{(aq)} \;+\; m\,H_2O \;=\; H_mX_{(aq)} \;+\; m\,OH^{-}{}_{(aq)}$$

Salts dissolved in water can change the pH of the solvent because of the hydrolysis reactions. As a result, hydrolysis of cations results acidic, while hydrolysis of anions results basic solutions (see equations above).

Quantitative evaluation of extension of the hydrolytic processes can be performed using the following relationship:

$$K_w = K_a \cdot K_b$$

The relationship shows that the product of acid and base ionization constants in aqueous solution for conjugate acid-base pairs equals the ion product of constant of water.

### VII.3.3 Common ion effect

According to the *Le Chatelier's principle*, if a system in a chemical equilibrium is altered by changing some condition, chemical reaction occurs to shift the equilibrium composition in a way that acts to reduce the effect of that change of condition. For example, when more product is added to an equilibrium mixture, thereby changing the concentration of reactant, net reaction occurs right to left (that is, in the reverse direction) to give a new equilibrium, and more reactants are produced. Such an observation is referred to as *common ion effect*.

For example, if acetate ion (e.g. sodium acetate) is added to an aqueous solution of acetic acid, dissociation of acetic acid is depressed and the pH of the solution becomes less acidic.

$$CH_3COOH_{(aq)} \;+\; H_2O \;\rightleftharpoons\; CH_3COO^{-}{}_{(aq)} \;+\; H_3O^{+}{}_{(aq)}$$

Similar relationship can be derived for weak bases:

$$NH_{3(aq)} \;+\; H_2O \;\rightleftharpoons\; NH_4^{+}{}_{(aq)} \;+\; OH^{-}{}_{(aq)}$$

If ammonium chloride is added to an aqueous solution of ammonia, the added ammonium ions make the solution more acidic (less basic).

Common ion effect can also be related to the heterogeneous equilibria. For example, in a saturated aqueous solution of an ionic compound of low solubility the heterogeneous equilibrium between the hydrated ions and the non-dissolved solid can be shifted by increasing concentration of any of the hydrated ions.

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Heterogeneous equilibria can be quantitatively characterized by the equilibrium constant for the solubility process

$$K_c = \frac{\left[Ag^{+}{}_{aq}\right]\left[Cl^{-}{}_{aq}\right]}{\left[AgCl_s\right]}$$

Because concentration of the solid remains constant, its concentration is normally combined with $K_c$ to give an equilibrium constant $K_{sp}$, which is called *solubility product*. Solubility product of a slightly soluble ionic compound equals the product of equilibrium concentrations of ions of the compound, each raised to the power equal to the number of such ions in the formula of the compound. Related to the above heterogeneous equilibrium:

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

According to the *Le Chatelier's principle*, if sodium chloride is added to the saturated silver chloride solution, silver chloride precipitate is to be formed. In other words, the solubility of the silver chloride (the concentration of its saturated solution) decreases by adding sodium chloride (chloride ions). The decrease of solubility of silver chloride on addition of sodium chloride is an example of the *common ion effect*.

### VII.3.4 Buffer solutions

The common ion effect has a special practical significance in relation to the so called buffer solutions. A *buffer solution* is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.

Buffers are solutions that contain:

a.) a weak acid and its conjugate base; or

b.) a weak base and its conjugate acid.

The function of buffers can be interpreted by means of the law of mass action. Suppose a buffer containing approximately equal molar amounts of a weak acid ( e.g. $CH_3COOH$) and its conjugate base ($CH_3COO^-$). In an aqueous solution of acetic acid partial dissociation of the weak acid takes place. Composition of the equilibrium mixture can be characterized by the ionization constant of acetic acid:

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^{-}_{(aq)} + H^{+}_{(aq)}$$

$$K_a = \frac{\left[CH_3COO^{-}\right]\left[H^{+}\right]}{\left[CH_3COOH\right]}$$

When adding sodium acetate, the salt completely dissociates:

$$CH_3COONa_{(s)} \longrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Thus, it can be considered that

$$[CH_3COO^-_{(aq)}] = [CH_3COONa]$$

The acetate ions added to the acetic acid solution depress dissociation of acetic acid. Such a change in composition can be explained in terms of the *Le Chatalier's principle*.

Thus, it can be considered that

$$[CH_3COOH]_{\text{unionized}} = [CH_3COOH]_{\text{initial}}$$

The hydrogen ion concentration can be expressed as follows:

$$K_a = \frac{[CH_3COONa][H^+]}{[CH_3COOH]_{\text{initial}}}$$

$$[H^+] = K_a \cdot \frac{[CH_3COOH]_{initial}}{[CH_3COONa]}$$

More generally

$$[H^+] = K_a \cdot \frac{[acid]}{[salt]}$$

Taking the negative logarithm of both sides, the equation can express pH of the buffer solution:

$$-\log[H^+] = -\log K_a - \log\frac{[acid]}{[salt]}$$

$$pH = pK_a - \log\frac{[acid]}{[salt]}$$

This is an equation relating the pH of a buffer at different concentrations of the conjugate acid and base. It is known as the *Henderson-Haselbach equation*.

Similar relation can be found for the pH of the buffer solutions containing a weak base (e.g. $NH_3$) and its conjugate acid ($NH_4^+$). (The latter can be added to the aqueous solution of ammonia in form of $NH_4Cl$.)

$$pOH = pK_b - \log\frac{[base]}{[salt]}$$

The pH resistance of the buffers against acids and bases is based on the reactions in which a large proportion of the added acids and bases are transformed to neutral particles.

### VII.3.5 Theory and practice of the acid-base titrations

„The basic idea of the *titrimetry*, that the quantity of an element or a compound can be determined, if an immediately reacting compound is added dropwise in a known strength, until the reaction takes place completely. The endpoint of the reaction can be detected easily as a well observable physical change (e.g. the change of the colour) (*Zechmeister-Faurholt-Gjaldbaek:* Chemical Practice)."

The volumetric (titrimetric) methods based on neutralisation reactions are still frequently used for the quantitative determination of inorganic acids and bases.

*Neutralisation reactions* meet all the criteria that make them suitable for volumetric analysis a.) the equivalent reagent quantities react stoichiometrically (there is no need for excess reagent) b.) there are no side reactions c.) the reaction is rapid (takes place during the titration period) d.) the endpoint of the titration can be detected. During measurements, solutions of acids (of unknown concentration) are titrated with standard solution of a strong base (acidimetry); or solutions of bases (of unknown concentration) are titrated with standard solution of a strong acid (alkalimetry).

#### VII.3.5.1 Titration curve

During an acid base titration the pH of the titrated mixture continuously changes. The pH of the solution can be determined at any point of the measurement. The pH of the titrated solution plotted against the added standard solution gives the *titration curve*.

The titration curve of determination of concentration of a hydrochloric acid solution with sodium hydroxide standard solution is shown on Fig. VII-1. The titration is based on the reaction of hydrochloric acid and sodium hydroxide:

$$NaOH + HCl = NaCl + H_2O$$

or, the more descriptive net-ionic equation:

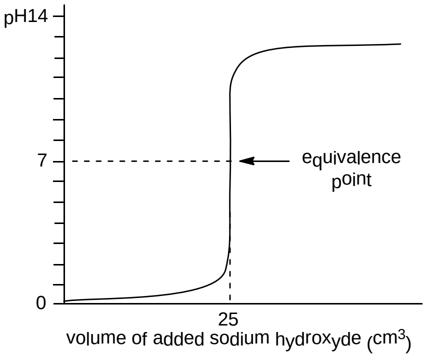
$$Na^+_{(aq)} + Cl^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} = Na^+_{(aq)} + Cl^-_{(aq)} + H_2O$$

Neutralisation reactions are based on combination of hydrogen ions (hydronium ions) and hydroxide ions to give water:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O$$

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2\,H_2O$$

**Figure VII-1.** Titration curve of titration of a strong acid with a strong base



While adding sodium hydroxide standard solution, initially the pH hardly changes, then increases steeply. The largest pH change can be observed in the region of the equivalence point, when addition of a relative small volume of the standard solution results in 5-6 unit change of the pH. The *equivalence point* is the point in the titration when stoichiometric amount of reactant has been added. Determination of concentration of a hydrochloric acid sample is based on the volume of the standard sodium hydroxide solution needed to reach the equivalence point.

### VII.3.5.2 Acid-base indicators

When the aim of a titration is determination of the equivalence point and not construction of the titration curve, the equivalence point can be detected by indicators. *Acid-base indicators* are weak organic acids or bases of which colours of the non-dissociated and the dissociated forms are different. Such indicators cause colour of the solution to change depending on the pH. The acid ionization equilibrium of a weak acid type acid-base indicator in aqueous solution as follows:

$$\underset{color_1}{HInd} + H_2O \rightleftharpoons H_3O^+ + \underset{color_2}{Ind^-}$$

The corresponding *equilibrium constant* is

$$K_{HInd} = \frac{[Ind^-][H^+]}{HInd}$$

The negative logarithm of this equilibrium constant is the *indicator exponent* (indicator constant). When

$$[H^+] = K_{Hind}$$

concentrations of the two forms of the indicator are equal:

$$[HInd] = [Ind^-]$$

The human eye is not sensitive enough to detect the point when the two forms of the indicator are present in the same concentrations. Eye is sensitive to colour changes over a range of concentration ratios of approximately 10. Thus, in case of a two-coloured indicator the clear colour of one of the forms can be recognized if the form counts at least 90 % of the indicator molecules. Accordingly, the transition range of the acid-base indicator is the pH range, where the $\frac{[Ind^-]}{[HInd]}$ value falls into the region between $\frac{1}{10}$ and $\frac{10}{1}$.

Thus, the transition range ($\Delta$pH) of a weak acid type (Hind) acid-bas indicator is

$$\Delta pH = pK_{HInd} \pm 1$$

while that of a weak base type (IndOH) acid-base indicator is

$$\Delta pOH = pK_{IndOH} \pm 1$$

To the correct selection of the indicator, the related titration curve is needed to be known. To detect the equivalence point, an indicator is to be chosen which has an *indicator exponent* near to the pH of the titrated solution at the equivalence point and its whole transition range overlaps the steep range of the titration curve.

Generally *methyl red* and *phenolphthalein* indicators are used. The endpoint range of methyl red is between pH 4.2 and pH 6.2. Below pH 4.4, it is red, and above pH 6.2 it is yellow. The endpoint range of phenolphthalein is between pH 8.2 and pH 10.0. Below pH 4.4, it is colourless, and above pH 6.2 it is red. In connection with phenolphthalein, it has to be mentioned that dissolved $CO_2$ disturbs the measurement; before end of titration the $CO_2$ has to be eliminated from the solution by boiling.

## VII.4 Practical task

### VII.4.1 Experimental task

#### VII.4.1.1 Acid-base equilibriums

In the following experiments a blank ("blind") test has to be made every case. Into a second test tube place the equal amount of distilled water and indicator instead of the test solution then add the reagent into both kinds of test tubes. The result has to be interpreted with the comparison of the experiment and the blank!

a. Add 2 drops of methyl red indicator to approximately 2 cm$^3$ of diluted acetic acid solution (gently homogenize the content of the test tube with shaking) and drop to the test tube concentrated sodium acetate solution until the colour of the indicator is going to be the same as the colour of the solution in the blank. Interpret the experiment!
b. Repeat the previous experiment but use diluted hydrochloric acid instead of acetic acid. Interpret the experiment!
c. In a test tube add 2-3 drops of thymolphthalein indicator to 3 cm$^3$ of ammonia solution, then the same quantity of ammonium chloride solution. Drop sodium hydroxide solution into the test tube until the colour of the indicator is going to be similar to the colour of the solution in the blank.
d. Place 5-5 cm$^3$ of ammonium acetate solution into two test tubes. To one of the test tubes add 2-3 drops of methyl red indicator and diluted hydrochloric acid solution, until the colour of the indicator becomes the same as the colour of the blank. Into the other test tube, after the addition of phenolphthalein indicator, add dropwise sodium hydroxide solution and finish the experiment as earlier. The solution functioning as a buffer with acids and bases. Interpret the experiment!

#### VII.4.1.2 Amphoteric equilibrium

In the following experiments the metal hydroxides are insoluble in water and some of them are amphoteric.

Alkalify 1 cm$^3$ solution of the zinc sulphate, alum ($KAl(SO_4)_2$), lead(II) nitrate, chrome alum ($KCr(SO_4)_2$) or the lead(II) chloride by sodium hydroxide solution until precipitate formation. Pour the supernatant of the deposited precipitate and continue dropwise addition of the base until the precipitate dissolves. Transfer a small portion of the solution into another test tube and carefully acidify it with diluted nitric acid. Precipitate forms again and dissolves in the excess of the acid.

As a comparison add sodium hydroxide solution in excess to the solution of an iron, copper, manganese or magnesium salt.

### VII.4.1.3 Hydrolysis of salts

a. Dilute some cm$^3$ of iron(III) chloride (originally strongly acidic) solution with distilled water until the precipitate appears in the solution. Afterwards add hydrochloric acid solution dropwise. Interpret the experiment!
b. Dilute 1 cm$^3$ of bismuth(III) chloride (originally strongly acidic) solution with distilled water until the precipitate appears in the solution. Afterwards add hydrochloric acid solution dropwise. Interpret the experiment with help of the next equation:

$$BiCl_3 + H_2O \leftrightarrow \underline{BiOCl} + 2\ HCl$$

c. Test the pH of aqueous solutions of the following salts with universal indicator: sodium hydrogen carbonate, sodium carbonate, ammonium sulphate, alum: $KAl(SO_4)_2$, sodium dihydrogen phosphate, trisodium phosphate. Interpret the experiment!

### VII.4.1.4 Heterogeneous equilibrium

a. Add barium chloride solution to a saturated calcium sulphate solution. Based on the observation, explain if $CaSO_4$ or $BaSO_4$ has got the higher $K_{sp}$ value?
b. Add such amount of ammonia solution to a small portion of magnesium sulphate solution that precipitate would appear in the solution. (Write equation of the reaction.) Then, add ammonium chloride solution until the precipitate dissolves. How can be explained dissolution of the precipitate?
c. Add silver nitrate solution to the sodium chloride solution, when silver chloride precipitate is formed. Let the precipitate to settle down and transfer the supernatant into another test tube and add potassium iodide solution to the supernatant. Explain the results considering solubility products of the silver halogenides.

### VII.4.1.5 Titration

#### VII.4.1.5.1. **Titration of a sulphuric acid solution of unknown concentration with sodium hydroxide standard solution**.

Sulphuric acid can be titrated with sodium hydroxide standard solution using *methyl red* indicator as a diprotic acid:

$$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2\ H_2O$$

Method of measurement

Pipette 10.00 cm$^3$ of sulphuric acid solution, containing approximately 50 mg of sulphuric acid, into a 100 cm$^3$ measuring flask. Dilute the solution to 30 cm$^3$ with distilled water and add 3-4 drops of methyl red indicator. Titrate it with a 0.1 M sodium hydroxide standard solution until appearance of the transient onion colour of the indicator. Three parallel measurements should be performed. Calculate the concentration of the sulphuric acid solution!

#### VII.4.1.5.2. **Titration of an acetic acid solution of unknown concentration with sodium hydroxide standard solution**.

Acetic acid is a weak monoprotic acid that can be titrated with sodium hydroxide in an aqueous solution. In this determination such an indicator should be used that has a colour change above pH 7, the pH corresponding to the pH of the aqueous solution of the forming salt (sodium acetate). For this reason *phenolphthalein* can be used as an indicator.

$$CH_3COOH + NaOH = CH_3COONa + H_2O$$

Method of measurement

Pipette 10.00 cm$^3$ of acetic acid solution, containing approximately 60 mg of acetic acid into a 100 cm$^3$ measuring flask. Dilute the solution to 30 cm$^3$ with distilled water and add 3-4 drops of phenolphthalein indicator to the solution. Titrate it with a 0.1 M sodium hydroxide standard solution until appearance of the pink colour of the indicator. After completion of the titration, the pink colour of the indicator should remain for 10-20 seconds. At the second and the third measurements, stop titration at about 0.5 cm$^3$ before the expected endpoint and boil the solution to expel carbon dioxide. While boiling add some pieces of boiling stone. After cooling back the solution, continue the titration until appearance of the pink colour of the indicator

## VII.4.2 Calculations

### VII.4.2.1 Dissociation of electrolytes

1. Calculate concentration of the hydrogen ions and the acetate ions in a 0.1 M aqueous acetic acid solution at 25 °C! The acid dissociation constant ($K_a$) is 1.85 $\cdot$ 10$^{-5}$ mol/dm$^3$. What is the degree of dissociation of acetic acid in the solution?

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Because $[H^+] = [CH_3COOH]$:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

Because $[CH_3COOH] \cong 0.1$ M

$$[H^+] = \sqrt{K_a \cdot 0.1} = \sqrt{1.86 \cdot 10^{-5} \cdot 10^{-1}}$$

$$[H^+] = 1.36 \cdot 10^{-3}$$

*Thus* $[H^+] = [CH_3COO^-] = 1.4 \cdot 10^{-3}$ *M.*

According to the definition

$$\alpha = \frac{\text{number of the dissociat ed moles}}{\text{number of the weighed moles}}$$

$$\alpha = \frac{[H^+]}{0.1} = \frac{1.4 \cdot 10^{-3}}{10^{-1}} = 1.4 \cdot 10^{-2}$$

*Thus, degree of dissociation in the acetic acid solution is* $1.4 \cdot 10^{-2}$*.*

2. Calculate the first dissociation constant of sulphurous acid if the pH of a 0.01 M solution of the acid is 2.16!

In the pH 2.16 solution

$$[H^+] = 10^{-2,16} = 6.92 \cdot 10^{-3}$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Because $[H^+] = [HSO_3^-]$

$$K_a = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = \frac{[H^+]^2}{[H_2SO_3]}$$

$$[H_2SO_3] = 0.010 - 6.92 \cdot 10^{-3} = 4.08 \cdot 10^{-3}$$

$$K_a = \frac{(6.92 \cdot 10^{-3})^2}{4.08 \cdot 10^{-3}} = \frac{4.79 \cdot 10^{-5}}{4.08 \cdot 10^{-3}} = 1.17 \cdot 10^{-2}\ \text{mol/dm}^3$$

*Thus, the first dissociation constant of sulphurous acid is* $1.2 \cdot 10^{-2}$ *mol/dm*$^3$*.*

3. Calculate the dissociation constant of the monoprotic weak acid of which 0.08 M solution’s pH is 2.7! What is the degree of dissociation of the acid in this solution?

$$HA \rightleftharpoons H^+ + A^-$$

Because $[H^+] = [A^-]$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$$

According to the definition: $[H^+] = 10^{-2.7} = 2.0 \cdot 10^{-3}$

$$K_a = \frac{(2.0 \cdot 10^{-3})^2}{0.08 - 2.0 \cdot 10^{-3}} = \frac{4.0 \cdot 10^{-6}}{0.078} = 5.13 \cdot 10^{-5}\ \text{mol/dm}^3$$

*Thus, the dissociation constant of the weak acid is* $5.1 \cdot 10^{-5}$ *mol/dm*$^3$*.*

The degree of dissociation of the weak acid:

$$\alpha = \frac{\text{number of dissociated moles}}{\text{number of weighed moles}}$$

$$\alpha = \frac{2.0 \cdot 10^{-3}}{0.08} = 0.025$$

*The degree of dissociation of the weak acid is 0.025.*

4. Calculate the mol/dm$^3$ concentration of an acetic acid solution of which pH equals to that of a 2.00 $\cdot$ 10$^{-4}$ M sulphuric acid solution! $K_a$ = 1,85 $\cdot$ 10$^{-5}$ mol/dm$^3$.

$$H_2SO_4 \rightarrow 2\ H^+ + SO_4^-$$

$$[H^+] = 2.00 \cdot 10^{-4} = 4.00 \cdot 10^{-4}\ M$$

$$pH = 3.40$$

The acetic acid, as a weak acid

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Because $[H^+] = [CH_3COO^-]$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

Supposed, that $[CH_3COOH]_{equlibrium} = [CH_3COOH]_{weighed}$

$$K_a = \frac{(4.00 \cdot 10^{-4})^2}{[CH_3COOH]_{weighed}}$$

$$[CH_3COOH]_{weighed} = \frac{(4.00 \cdot 10^{-4})^2}{1.85 \cdot 10^{-5}} = \frac{16.00 \cdot 10^{-8}}{1.85 \cdot 10^{-5}} = 8.65 \cdot 10^{-3}\ M$$

*Thus, concentration of the acetic acid solution is 8.7 · 10$^{-3}$ M.*

5. Calculate the mol/dm$^3$ concentration of the magnesium and chloride ions in a 6.0 $\cdot$ 10$^{-3}$ M $MgCl_2$ solution! What is the ionic strength of the solution?

Supposing complete dissociation:

$$[Mg^{2+}] = 6.0 \cdot 10^{-3}\ M$$

$$[Cl^-] = 12.0 \cdot 10^{-3}\ M$$

The ionic strength of the solution:

$$I = \frac{6.0 \cdot 10^{-3} \cdot 4 + 12.0 \cdot 10^{-3} \cdot 1}{2} = \frac{0.024 + 0.012}{2} = 0.018\ M$$

*Thus, ionic strength of the solution is 0,018 M.*

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co-financed by the European Social Fund

6. Calculate the m/V% concentration of an ammonia solution of pH 10.70! $K_b = 1.79 \cdot 10^{-5}$ mol/dm$^3$
7. Calculate the percentage of dissociation in a 0.1 M aqueous acetic acid solution! $K_a = 1.85 \cdot 10^{-5}$ mol/dm$^3$
8. Calculate the mol/dm$^3$ concentration of an ammonia solution in which the degree of dissociation is 0.5 %! $K_b = 1.19 \cdot 10^{-5}$ mol/dm$^3$
9. The degree of dissociation in a 0.375 M aqueous hydrogen cyanide solution is $3.57 \cdot 10^{-3}$ %. Calculate the dissociation constant of the acid ($K_a$)!
10. The anion concentration in a 0.01 M hydrogen fluoride solution is $7.6 \cdot 10^{-3}$ mol/dm$^3$. What extent the solution should be diluted to achieve 90 % degree of dissociation?

### VII.4.2.2 Hydrogen ion concentration

1. Calculate the pH of a 0.050 M hydrochloric acid solution at 25 °C!

Supposing complete dissociation:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$[H^+] = 0.05 \text{ M}$$

$$pH = -\log 0.05 = 1.30$$

*Thus, the pH of the solution is 1.30.*

2. Calculate the pH of a 0.44 m/V% sodium hydroxide solution at 25 °C! M(NaOH) = 40.0 g/mol

Supposing complete dissociation:

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

| | |
|---|---|
| 100 cm$^3$ of solution | 0.44 g of NaOH |
| 1000 cm$^3$ of solution | x g of NaOH |

$$x = 4.4 \text{ g}$$

| | |
|---|---|
| 1 mol NaOH | 40 g |
| x mol NaOH | 4.4 g |

$$x = \frac{4.4}{40} = 0.11\,mol$$

Thus $$[NaOH] = [OH^-] = 0.11 \text{ mol}$$

$$pOH = -\log [OH^-] = -\log 0.11 = 0.96$$

$$pH = 14-0.96 = 13.04$$

*Thus, the pH of the solution is 13.04.*

3. Calculate the ion product constant of water at 32 °C if the pH of a $2.0 \cdot 10^{-2}$ M NaOH solution is 12.05?

According to definition:

$$[H^+] = 10^{-12.05} = 8.91 \cdot 10^{-13}\ \mathrm{M}$$

Supposing complete dissociation:

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$[OH^-] = [NaOH] = 2.0 \cdot 10^{-2}\ \mathrm{M}$$

*The ion product constant of water:*

$$K_w = 8.91 \cdot 10^{-13} \cdot 2.0 \cdot 10^{-2} = 1.78 \cdot 10^{-14}\ \mathrm{mol^2/dm^6}$$

*Thus, the ion product constant of water at 32 °C is* $1.78 \cdot 10^{-14}\ mol^2/dm^6$.

4. Calculate the pH of a 0.12 m/V% acetic acid solution! $K_a = 1.85 \cdot 10^{-5}$ mol/dm$^3$, $M(CH_3COOH) = 60.01$ g/mol

| | |
|---|---|
| 100 cm$^3$ of solution | 0.120 g of acetic acid |
| 1000 cm$^3$ of solution | x g of acetic acid |

x = 1.20 g

| | |
|---|---|
| 1 mol acetic acid | 60.01 g |
| x mol acetic acid | 1.20 g |

$$x = \frac{1.20 \cdot 1}{60.01} = 0.020\, mol$$

The dissociation of the acetic acid:

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

| | | | |
|---|---|---|---|
| Initial concentration | 0,020 | - | - |
| Equilibrium concentration | 0.020 - x | x | x |

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x \cdot x}{0.020 - x}$$

Considering weak dissociation of acetic acid:

$$[CH_3COOH]_{equilibrium} \cong [CH_3COOH]_{initial}$$

$$K_a = \frac{x^2}{0.020} = 1.85 \cdot 10^{-5}\ \mathrm{mol/dm^3}$$

$$x = \sqrt{1.85 \cdot 10^{-5} \cdot 0.020} = \sqrt{3.7 \cdot 10^{-7}} = 6.08 \cdot 10^{-4}\ \mathrm{M}$$

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

$$pH = -\log 6.08 \cdot 10^{-4} = 3.2$$

*Thus, the pH of the acetic acid solution is 3.2.*

5. Calculate the m/V% concentration, the mol/dm$^3$ concentration and the normal concentration (N) of a sulphuric acid solution of pH 2.30! M($H_2SO_4$) = 98.0 g/mol

Supposed that the sulphuric acid dissociates completely:

$$H_2SO_{4(aq)} \rightarrow 2\ H^+_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$[H^+] = 2 \cdot [H_2SO_4]$$

Based on definition:

$$[H^+] = 10^{-2.30} = 5.01 \cdot 10^{-3}\ M$$

Thus:

$$\left[H_2SO_4\right] = \frac{5.01 \cdot 10^{-3}}{2} = 2.505 \cdot 10^{-3}\ M$$

*Thus, the mol/dm$^3$ concentration of the solution is 2.51 · 10$^{-3}$ M.*

Because 1 mole of $H_2SO_4$ = 2 equivalents of $H_2SO_4$, the normal concentration of the solution is:

$$c = 2 \cdot 2.505 \cdot 10^{-3} = 5.01 \cdot 10^{-3}\ N$$

*Thus, the normal concentration of the solution is 5.01 · 10$^{-3}$ N.*

1000 cm$^3$ of solution    2.505 · 10$^{-3}$ mol
100 cm$^3$ of solution    x mol

$$x = 2.505 \cdot 10^{-4}\ mol$$

1 mol $H_2SO_4$    98.0 g
2.505 · 10$^{-4}$ mol $H_2SO_4$    x g

$$x = 2.505 \cdot 10^{-4} \cdot 98.0 = 0.0245\ g$$

*Thus, the m/V% concentration of the solution is 0.025 m/V%.*

6. What amount (mg) of HCl is there in 1 cm$^3$ volume of a solution of pH 1.8? M(HCl) = 36.46 g/mol
7. Calculate the pH of a 0.005 M sulphuric acid solution!
8. Calculate the pH of a 0.005 M sulphurous acid solution! ($K_a$ = 1.54 · 10$^{-2}$ mol/dm$^3$)
9. Calculate the pH of a 0.05 M ammonia solution! ($\alpha$ = 0.012; $K_b$ = 1.79 · 10$^{-5}$ mol/dm$^3$)
10. Calculate the percentage of ionization in a 0.1 M hydrogen fluoride solution of pH 2.24!
11. What amount of sodium hydroxide is there in 200.0 cm$^3$ volume of solution of which pH equals to that of a 0.1 M ammonia solution? ($K_b$ = 1.79 · 10$^{-5}$ mol/dm$^3$)
12. Calculate the pH of a 0.15 M acetic acid solution! ($K_a$ = 1.85 · 10$^{-5}$ mol/dm$^3$)
13. What extent a 0.01 M acetic acid solution should be diluted to shift the pH by 1 unit? ($K_a$ = 1.85 · 10$^{-5}$ mol/dm$^3$)

14. 100 cm$^3$ of 2.0 m/V% sulphuric acid solution is diluted up to 500 cm$^3$. Calculate the pH of the diluted solution! M($H_2SO_4$) = 98.08
15. What ratio the hydrochloric acid solutions of pH 3.0 and pH 5.0 should be mixed to obtain a solution of pH 4.0?

### VII.4.2.3 Hydrolysis

1. Calculate the pH of a 0.01 M aqueous solution of sodium acetate! $K_a = 1.85 \cdot 10^{-5}$ mol/dm$^3$

The acetate ions react with water:

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

The base ionization constant of the acetate ion:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_b = \frac{K_v}{K_a} = \frac{1.0{\cdot}10^{-14}}{1.85{\cdot}10^{-5}} = 5.41{\cdot}10^{-10}$$

because $[CH_3COOH] = [OH^-]$, and

$$[CH_3COO^-]_{\text{initial}} \approx [CH_3COO^-]_{\text{equilibrium}}$$

$$K_b = \frac{[OH^-]^2}{0.01} = 5.41{\cdot}10^{-10}$$

$$[OH^-] = \sqrt{5.41{\cdot}10^{-10}\ \ 1.0\cdot10^{-2}} = 2.33{\cdot}10^{-4}$$

$$\text{pOH} = -\log 2.33 \cdot 10^{-4} = 3.63$$

$$\text{pH} = 14.0 - 3.63 = 10.37$$

*Thus, the pH of the solution is 10.4.*

2. Calculate the pH of a 0.10 M aqueous solution of potassium cyanide! $K_a = 6.2 \cdot 10^{-10}$ mol/dm$^3$

The cyanide ions react with water:

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

The base ionization constant of the cyanide ion:

$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

thus

$$K_b = \frac{K_v}{K_a} = \frac{1.0 \cdot 10^{-14}}{6.2 \cdot 10^{-10}} = 1.6 \cdot 10^{-5} \text{ mol/dm}^3$$

because $[HCN]_{aq} = [OH^-]$, and

$$[CN^-]_{inital} \cong [CN^-]_{equilibrium}$$

$$K_b = \frac{[OH^-]^2}{0.10} = 1.6 \cdot 10^{-5} \text{ mol/dm}^3$$

$$\left[OH^-\right] = \sqrt{0.10 \cdot 1.6 \cdot 10^{-5}} = 1.26 \cdot 10^{-3} \text{ M}$$

$$\text{pOH} = -\log [OH^-] = -\log 1.26 \cdot 10^{-3} = 2.90$$

$$\text{pH} = 14.0 - 2.90 = 11.10$$

*Thus, the pH of the solution is 11.1.*

3. The extent of hydrolysis in a 0.040 M aqueous solution of NaOCl is 0.22 %. Calculate the concentration of the particles in the solution! $K_a = 3.7 \cdot 10^{-8}$ mol/dm$^3$

   The hypochlorite ions react with water:

$$OCl^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]}$$

Because $[OH^-] = [HOCl]$, and

$$[OCl^-]_{initial} \cong [OCl^-]_{equilibrium}$$

Since

$$\text{\% of hydrolysis} = \frac{[HOCl]}{0.040} \cdot 100 = 0.22$$

*Thus, concentrations of the particles in the solution are*:

$$[HOCl] = \frac{0.22 \cdot 0.040}{100} = 8.8 \cdot 10^{-5}\ M$$

$$[OH^-] = [HOCl] = 8.8 \cdot 10^{-5}\ M \text{ , and}$$

$$[OCl^-] \cong 0.04 \text{ M}$$

4. Calculate the mol/dm$^3$ concentration of a potassium formiate solution of pH 9.21! $K_a = 1.77 \cdot 10^{-4}$ mol/dm$^3$

   The formiate ions react with water:

$$HCOO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

$$K_b = \frac{K_v}{K_a} = \frac{1.0 \cdot 10^{-14}}{1.77 \cdot 10^{-4}} = 5.65 \cdot 10^{-11} \text{ mol/dm}^3$$

Based on the pH of the solution:

$$\text{pOH} = 14.0 - 9.21 = 4.79$$

$$[\text{OH}^-] = 10^{-4.79} = 1.62 \cdot 10^{-5}$$

because $[\text{OH}^-] = [\text{HCOOH}]$, and

$$[\text{HCOO}^-]_{\text{initial}} \cong [\text{HCOO}^-]_{\text{equilibrium}}$$

$$K_b = \frac{[OH^-]^2}{[HCOO^-]}$$

$$[HCOO^-] = \frac{K_b}{[OH^-]^2} = \frac{5.65 \cdot 10^{-11}}{(1.62 \cdot 10^{-5})^2} = \frac{5.65 \cdot 10^{-11}}{2.62 \cdot 10^{-10}} = 2.16 \cdot 10^{-1} = 0.216 \text{ M}$$

*Thus, concentration of the potassium formiate solution is 0.22 M.*

5. Calculate the pH of a 0.050 M aqueous ammonium sulphate solution! $K_b = 1.79 \cdot 10^{-5}$ mol/dm$^3$

   The ammonium ions react with water:

$$\text{NH}_4^+{}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_{3(aq)} + \text{H}_3\text{O}^+{}_{(aq)}$$

   The acid ionization constant of the ammonium ions:

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$K_a = \frac{K_v}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.79 \cdot 10^{-5}} = 5.59 \cdot 10^{-10}$$

   Because $[\text{NH}_3] = [\text{H}^+]$, and

$$[\text{NH}_4^+]_{\text{initial}} \cong [\text{NH}_4^+]_{\text{equilibrium}} = 0.10 \text{ M}$$

$$K_a = \frac{[H^+]^2}{[NH_4^+]} = \frac{[H^+]^2}{0.10}$$

$$[H^+] = \sqrt{5.59 \cdot 10^{-10} \cdot 0.10} = 7.48 \cdot 10^{-6} \text{ M}$$

$$\text{pH} = -\log 7.48 \cdot 10^{-6} = 5.13$$

   *Thus, the pH of the solution is 5.13.*

6. Calculate the pH of a 0.050 M sodium carbonate solution? $K_{a1} = 4.3 \cdot 10^{-7}$ mol/dm$^3$, $K_{a2} = 5.6 \cdot 10^{-11}$ mol/dm$^3$
7. Calculate the pH of a 0.050 M benzoic acid and a 0.050 M sodium benzoate solution! $K_a = 6.3 \cdot 10^{-5}$ mol/dm$^3$

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8. The pH of a 0.020 M sodium phenolate solution is 11.10. Calculate the acid dissociation constant of phenol!
9. The pH of a 12.0 m/V% sodium salicylate solution is 8.42. Calculate the acid dissociation constant of salicylic acid! $M(C_7H_5NaO_3) = 160.1$ g/mol
10. Calculate the amount of sodium acetate (in moles) that is needed to prepare 500.0 $cm^3$ solution of pH 8.89? $K_a = 1.85 \cdot 10^{-5}$ $mol/dm^3$

### VII.4.2.4 Calculations on solubility

1. What volume of water (in $dm^3$) is needed to dissolve 1.00 g of $BaSO_4$? $K_{sp} = 1.00 \cdot 10^{-10}$ $mol^2/dm^6$. $M(BaSO_4) = 233,4$

Because $[Ba^{2+}{}_{(aq)}] = [SO_4{}^{2-}{}_{(aq)}]$

$$K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = [Ba^{2+}]^2 = 1.0 \cdot 10^{-10}$$

thus: $[Ba^{2+}] = [SO_4{}^{2-}] = 1.00 \cdot 10^{-5}$ M

| | |
|---|---|
| 1 mol $BaSO_4$ | 233.4 g |
| x mol $BaSO_4$ | 1.00 g |

$$x = \frac{1.00}{233.4} = 4.28 \cdot 10^{-3}\,\mathrm{mol}$$

| | |
|---|---|
| 1.00 $dm^3$ water dissolves | $1.00 \cdot 10^{-5}$ mol $BaSO_4$ |
| x $dm^3$ water dissolves | $4.28 \cdot 10^{-3}$ mol $BaSO_4$ |

$$x = \frac{4.28 \cdot 10^{-3} \cdot 1.00}{1.00 \cdot 10^{-5}} = 428\,\mathrm{dm}^3$$

*Thus, 428 $dm^3$ water is needed to dissolve 1.00 g $BaSO_4$.*

2. 0.312 g of magnesite ($MgCO_3$) can be dissolved in 400.0 $cm^3$ of water. Calculate the solubility product of $MgCO_3$! $M(MgCO_3) = 84,3$ g/mol

| | |
|---|---|
| 400.0 $cm^3$ water dissolves | 0.312 g $MgCO_3$ |
| 1000.0 $cm^3$ water dissolves | x g $MgCO_3$ |

$$x = \frac{1000.0 \cdot 0.312}{400.0} = 0.78g$$

| | |
|---|---|
| 1 mol $MgCO_3$ | 84.3 g |
| x mol $MgCO_3$ | 0.78 g |

$$x = \frac{0.78 \cdot 1}{84.3} = 9.25 \cdot 10^{-3}mol$$

$$MgCO_{3(s)} \rightleftharpoons Mg^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$K_{sp} = [Mg^{2+}] \cdot [SO_4{}^{2-}] = [Mg^{2+}]^2$$

$$K_{sp} = (9.25 \cdot 10^{-3}) \cdot (9.25 \cdot 10^{-3}) = 8.56 \cdot 10^{-5}\ mol^2/dm^6$$

*Thus, the solubility product of the $MgCO_3$ is $8.56 \cdot 10^{-5}$ $mol^2/dm^6$.*

3. 200.0 cm$^3$ of saturated $Ag_3PO_4$ solution contains 130.0 mg of dissolved salt. Calculate the solubility product of the compound! $M(Ag_3PO_4) = 418.6$ g/mol

| | |
|---|---|
| 1 mmol $Ag_3PO_4$ | 418.6 mg |
| x mmol $Ag_3PO_4$ | 130.0 mg |

$$x = \frac{130.0 \cdot 1}{418.6} = 0.31\,\mathrm{mmol}$$

| | |
|---|---|
| 200.0 cm$^3$ solution dissolves | 0.31 mmol $Ag_3PO_4$ |
| 1000 cm$^3$ solution dissolves | x mmol $Ag_3PO_4$ |

$$x = \frac{0.31 \cdot 1000}{200.0} = 1.55\,\mathrm{mmol} = 1.55 \cdot 10^{-3}\,\mathrm{mol}$$

| $Ag_3PO_{4(s)}$ | $\rightarrow$ | $3\ Ag^+_{(aq)}$ | + | $PO_4{}^{3-}{}_{(aq)}$ |
|---|---|---|---|---|
| 1 mol | | 3 mol | | 1 mol |
| $1.55 \cdot 10^{-3}$ mol | | $4.65 \cdot 10^{-3}$ mol | | $1.55 \cdot 10^{-3}$ mol |

$$K_{sp} = [Ag^+]^3\,[PO_4{}^{3-}]$$

$$K_{sp} = (4.65 \cdot 10^{-3})^3\,(1.55 \cdot 10^{-3}) = 1.00 \cdot 10^{-7} \cdot 1.55 \cdot 10^{-3} = 1.55 \cdot 10^{-10}\ \mathrm{mol^4/dm^{12}}$$

*Thus, the solubility product of the silver phosphate is* $1.55 \cdot 10^{-10}$ *mol*$^4$*/dm*$^{12}$*.*

4. Will $Ag_2SO_4$ precipitate be formed if 1.00 dm$^3$ of 0.10 M $AgNO_3$ solution is mixed with 0.20 cm$^3$ of 49.0 m/m% sulphuric acid solution? Density of the sulphuric acid solution is 1.380 g/cm$^3$. $K_{sp} = 7.70 \cdot 10^{-5}$ mol$^3$/dm$^9$; $M(H_2SO_4) =$ 98,0 g/mol

| | |
|---|---|
| 1.00 cm$^3$ of sulphuric acid solution | 1.380 g |
| 0.20 cm$^3$ of sulphuric acid solution | x g |

$$x = \frac{0.20 \cdot 1.380}{1.00} = 0.276\,g$$

| | |
|---|---|
| 100.0 g of sulphuric acid solution | 49.0 g $H_2SO_4$ |
| 0.276 g of sulphuric acid solution | x g $H_2SO_4$ |

$$x = \frac{0.276 \cdot 49.0}{100.0} = 0.135\,g$$

| | |
|---|---|
| 98.0 g of $H_2SO_4$ | 1 mol |
| 0.135 g of $H_2SO_4$ | x mol |

$$x = \frac{0.135 \cdot 1}{98.0} = 0.138 \cdot 10^{-3}\ \mathrm{mol}$$

Thus, the mol/dm$^3$ concentration of the sulphuric acid solution:

| | |
|---|---|
| 0.20 cm$^3$ of solution | $1.38 \cdot 10^{-4}$ mol $H_2SO_4$ |
| 1000 cm$^3$ of solution | x mol $H_2SO_4$ |

$$x = \frac{1.38 \cdot 10^{-4} \cdot 10^{3}}{0.20} = 6.9 \cdot 10^{-1} \text{ M}$$

Neglecting change of volume while mixing the solutions:

$$[Ag^+] = 10^{-1} \text{ M}$$

Considering the dilution of the sulphuric acid solution:

$$c_1 \cdot V_1 = c_o \cdot V_o$$

$$6.9 \cdot 10^{-1} \cdot 0.20 = c_0 \cdot 1000.20$$

$$c_o = \frac{6.9 \cdot 10^{-1} \cdot 0.20}{1000.20} = 1.38 \cdot 10^{-4}\, M$$

$$c_0 = 1.38 \cdot 10^{-4} \text{ M}$$

*Thus,* $[SO_4^{2-}] = 1.38 \cdot 10^{-4}$ *M*

The product of ion concentrations raised to the appropriate powers:

$$L = [Ag^+]^2 \left[SO_4^{2-}\right] = (1.0 \cdot 10^{-1})^2 \cdot 1.38 \cdot 10^{-4} = 1.38 \cdot 10^{-6} \text{ mol}^3/\text{dm}^9$$

*Because the ion product ($1.38 \cdot 10^{-6}$ mol$^3$/dm$^9$) of the silver and sulphate ions is lower than the solubility product of $Ag_2SO_4$ ($7.70 \cdot 10^{-5}$ mol$^3$/dm$^9$), no precipitate formation occurs in the solution.*

5. Calculate the solubility of AgBr in a $5.0 \cdot 10^{-3}$ M KBr solution! $K_{sp} = 6.4 \cdot 10^{-13}$ mol$^2$/dm$^6$
6. What amount of AgOH (in mg) can be dissolved in 1.0 dm$^3$ of pH 13 sodium hydroxide solution at 18 °C? $K_{sp}(AgOH) = 1.52 \cdot 10^{-8}$ mol$^2$/dm$^6$, M(AgOH) = 124.9 g/mol
7. Calculate the pH of the solution, which is made by dissolving 0.10 g of $Ca(OH)_2$ in 1.0 dm$^3$ of water! $K_{sp}(Ca(OH)_2) = 5.5 \cdot 10^{-6}$ mol$^3$/dm$^9$
8. What volume (in dm$^3$) of water is needed to dissolve 1.0 g of $BaSO_4$? $K_s = 1.1 \cdot 10^{-10}$ mol$^2$/dm$^6$. $M(BaSO_4) = 233.4$ g/mol
9. 10.0 dm$^3$ of saturated $Pb_3(PO_4)_2$ solution dissolves 1.38 mg of salt. How many times will be its solubility reduced if 1.64 g of $Na_3PO_4$ is added to the solution? $M(Pb_3(PO_4)_2) = 811.5$ g/mol
10. Calculate the solubility product of cadmium hydroxide if the pH of its saturated solution is 9.23!
11. Calculate the highest concentration of calcium ions in a 0.01 M sodium fluoride solution! $K_{sp}(CaF_2) = 5 \cdot 10^{-11}$ mol$^3$/dm$^9$.
12. Calculate the solubility of calcium hydroxide in a 0.10 M $Ba(OH)_2$ solution! $K_{sp}(Ca(OH)_2) = 5.5 \cdot 10^{-6}$ mol$^3$/dm$^9$.

13. Will $Ag_2SO_4$ precipitate be separated from a saturated AgBr solution if solid sodium sulphate is added to set the sulphate ion concentration to 0.003 mol/dm$^3$? (Dilution can be neglected.) $K_{sp}$ ($Ag_2SO_4$) = $7.7 \cdot 10^{-5}$ mol$^3$/dm$^9$ , $K_{sp}$ (AgBr) = $5.6 \cdot 10^{-13}$ mol$^2$/dm$^6$
14. Will $BaSO_4$ precipitate be formed if 10.0 cm$^3$ of saturated $CaSO_4$ solution (of 0.148 g/dm$^3$ concentration) is mixed with 10.0 cm$^3$ of 0.01 M $Ba(NO_3)_2$ solution? $K_{sp}$ ($BaSO_4$) $1.1 \cdot 10^{-10}$ mol$^2$/dm$^6$.
15. Calculate the pH of the saturated $Mg(OH)_2$ solution at 20 °C if the solution is made by dissolution of 1.90 g of $MgCl_2$ in 1.0 dm$^3$ of water. $K_{sp}(Mg(OH)_2) = 5.61 \cdot 10^{-12}$ mol$^3$/dm$^9$, $M(MgCl_2) = 95.21$ g/mol

### VII.4.2.5 Buffers

1. Calculate the pH of a solution containing 0.005 M acetic acid and $5.0 \cdot 10^{-4}$ M sodium-acetate! $K_a = 1.85 \cdot 10^{-5}$ mol/dm$^3$.

Based on the *Henderson-Hasselbach* equation:

$$pH = pK_s + \log \frac{[acetate]_{initial}}{[acetic\ acid]_{initial}}$$

$$pK_s = -\log 1.85 \cdot 10^{-5} = 4.73$$

$$pH = 4.73 + \log \frac{5.0 \cdot 10^{-4}}{5.0 \cdot 10^{-3}}$$

$$pH = 4.73 + \log 10^{-1}$$

$$pH = 3.73$$

*Thus, the pH of the mixture is 3.73.*

2. Calculate the pH of a solution containing 0.050 M $NH_3$ and 0.050 M $NH_4Cl$! $K_b = 1.79 \cdot 10^{-5}$ mol/dm$^3$

Based on the *Henderson-Hasselbach* equation:

$$pOH = pK_b + \log \frac{[ammonium - ion]_{initial}}{[ammonia]_{initial}}$$

$$pK_b = -\log 1.79 \cdot 10^{-5} = 4.75$$

$$pOH = 4.75 + \log \frac{0.050}{0.050}$$

$$pOH = 4.75$$

$$pH = 14 - 4.75 = 9.25$$

*Thus, the pH of the solution is 9.25.*

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3. Calculate the acetate/acetic acid ratio in an acetic acid/ sodium-acetate buffer of pH 4.30! $K_a = 1{,}85 \cdot 10^{-5}$ mol/dm$^3$

   Based on the *Henderson-Hasselbach* equation:

   $$pH = pK_a + \log \frac{[acetate]_{initial}}{[acetic\ acid]_{initial}}$$

   $$pK_s = -\log 1.85 \cdot 10^{-5} = 4.73$$

   $$4{,}30 = 4{,}73 + \log \frac{[acetate]_{initial}}{[acetic\ acid]_{initial}}$$

   $$-0.43 = \log \frac{[acetate]_{initial}}{[acetic\ acid]_{initial}}$$

   $$0.37 = \frac{[acetate]_{initial}}{[acetic\ acid]_{initial}}$$

   *Thus, the ratio of acetate to acetic acid is 0.37:1.*

4. What a formiate/formic acid ratio is needed to prepare a formic acid/sodium-formiate buffer of pH 3.30? $K_a = 1.78 \cdot 10^{-4}$ mol/dm$^3$

   $$pH = pK_s + \log \frac{[formiate]_{initial}}{[formic\ acid]_{initial}}$$

   $$pK_s = -\log 1.78 \cdot 10^{-4} = 3.75$$

   $$3.30 = 3.75 + \log \frac{[formiate]_{initial}}{[formic\ acid]_{initial}}$$

   $$-0.45 = \log \frac{[formiate]_{initial}}{[formic\ acid]_{initial}}$$

   $$0.35 = \frac{[formiate]_{initial}}{[formic\ acid]_{initial}}$$

   *Thus, the necessary ratio of acetate to acetic acid is 0.35:1.*

5. 10.0 $cm^3$ of 0.20 M sodium acetate solution is added to 10.0 $cm^3$ of 0.30 M acetic acid solution. Calculate the pH of the obtained solution! Calculate the pH change resulted in addition of 5.00 $cm^3$ of 0.10 M NaOH solution! $K_a = 1,85 \cdot 10^{-5}$ $mol/dm^3$

The concentrations of the solutes are halved, when mixing the two solutions. In the forming mixture:

$$[CH_3COONa] = 0.10\ M$$

$$[CH_3COOH] = 0.15\ M$$

$$pK_a = -\log 1.85 \cdot 10^{-5} = 4.73$$

According to the *Henderson-Hasselbach* equation:

$$pH = pK_s + \log \frac{[acetate]_{initial}}{[acetic\ acid]_{initial}}$$

$$pH = 4.73 + \log \frac{0.10}{0.15}$$

$$pH = 4.73 + \log 0.67 = 4.73 - 0.18$$

$$pH = 4.55$$

*Thus, the pH of the obtained solution is 4.55.*

In 10.0 $cm^3$ 0.20 M sodium acetate solution: $10.0 \cdot 0.20 = 2.00$ mmol sodium acetate;

in 10.0 $cm^3$ 0.30 M acetic acid solution: $10.0 \cdot 0.30 = 3.00$ mmol acetic acid; and

in 5.00 $cm^3$ 0.10 M sodium hydroxide solution: $5.00 \cdot 0.10 = 0.50$ mmol sodium hydroxide can be found.

The pH after of addition of the sodium hydroxide solution:

$$pH = 4.73 + \log \frac{2.00 + 0.50}{3.00 - 0.50}$$

$$pH = 4.73 + \log \frac{2.50}{2.50}$$

$$pH = 4.73$$

*Thus, the pH of the mixture (buffer) after addition of the sodium hydroxide solution is 4.73.*

6. 40.0 $cm^3$ of 0.8 M sodium formiate solution is added to 40.0 $cm^3$ of 1.2 M formic acid solution. Calculate the pH of the obtained solution! Calculate the pH change resulted in addition of 20.0 $cm^3$ 0.4 M NaOH solution! $K_a = 1.78 \cdot 10^{-4}$ $mol/dm^3$
7. 20.0 $cm^3$ of 0.4 M sodium acetate solution is added to 20.0 $cm^3$ of 0.6 M acetic acid. Calculate the pH of the obtained solution! Calculate the pH change resulted in addition of 10.0 $cm^3$ of 0.1 M $HNO_3$ solution! $K_a = 1.85 \cdot 10^{-5}$ $mol/dm^3$

8. In what a volume ratio 1.0 M ammonia and the 1.0 M ammonium chloride solutions have to be mixed to obtain a solution of pH 8.50? $K_b = 1.79 \cdot 10^{-5}$ mol/dm$^3$
9. What proportion the degree of dissociation of a 0.10 M formic acid solution is reduced if 0.05 mol of sodium formiate is dissolved in 1 dm$^3$ of the solution? $K_s = 1.78 \cdot 10^{-4}$ mol/dm$^3$
10. The pH of an aqueous solution containing hydrogen cyanide and potassium cyanide of the equal concentrations is 9.32. Calculate the acid dissociation constant of hydrogen cyanide!

### VII.4.2.6 Acid-base titrations

1. For titration of precisely weighed 0.1979 g of potassium hydrogen carbonate 20.00 cm$^3$ of approximately 0.1 M hydrochloric acid solution was consumed. Calculate the exact concentration of the hydrochloric acid solution! M($KHCO_3$) = 100.12 g/mol

The equation for which the determination is based on:

$$KHCO_3 + HCl = KCl + CO_2 + H_2O$$

1 mol $KHCO_3$ 100.12 g
x mol $KHCO_3$ 0.1979 g

$$x = \frac{0.1979}{100.12} = 1.977 \cdot 10^{-3}\,\text{mol}$$

Because 1 mole $KHCO_3$ reacts with 1 mole HCl:

20 cm$^3$ of standard solution 1.977 · 10$^{-3}$ mol HCl
1000.00 cm$^3$ of standard solution x mol HCl

$$x = \frac{1.977 \cdot 10^{-3} \cdot 1000.00}{20.00} = 0.09885\,\text{mol}$$

*Thus, the exact concentration of the hydrochloric acid solution is 0.0989 M.*

2. For titration of 5.00 cm$^3$ wine-vinegar sample 35.00 cm$^3$ of 0.1000 M sodium hydroxide standard solution was consumed. Calculate the acetic acid content of the sample! M($CH_3COOH$)= 60.05 g/mol

The equation that serves as base for the determination:

$CH_3COOH + NaOH = CH_3COONa + H_2O$

1000.00 cm$^3$ of standard solution 0.1000 mol NaOH
35.00 cm$^3$ of standard solution x mol NaOH

$$x = \frac{35.00 \cdot 0.1000}{1000.00} = 3.5 \cdot 10^{-3}\,\text{mol}$$

Because 1 mole acetic acid reacts with 1 mole of sodium hidroxide:

there is $3.5 \cdot 10^{-3}$ mol acetic acid in the 5.00 $cm^3$ of wine-vinegar sample

| | |
|---|---|
| 1 mol acetic acid | 60.05 g |
| $3.5 \cdot 10^{-3}$ mol acetic acid | x g |

$$x = 60.05 \cdot 3.5 \cdot 10^{-3} = 0.210 \text{ g}$$

*Thus, there is 0.210 g acetic acid in the 5.0 $cm^3$ wine-vinegar sample.*

3. For titration of 10.00 $cm^3$ ammonia solution 7.35 $cm^3$ of 0.0488 M sulphuric acid standard solution was consumed. Calculate the nitrogen (N) content of the ammonia sample! M(N) = 14.01 g/mol

   The equation that serves as base for the determination:

   $2\ NH_3 + H_2SO_4 = (NH_4)_2SO_4$

| | |
|---|---|
| 1000.00 $cm^3$ of $H_2SO_4$ standard solution | 0.0488 mol $H_2SO_4$ |
| 7.35 $cm^3$ of $H_2SO_4$ standard solution | x mol $H_2SO_4$ |

$$x = \frac{7.35 \cdot 0.0488}{1000.00} = 3.59 \cdot 10^{-4}\ mol$$

Because 1 mole sulphuric acid reacts with 2 moles of ammonia:

In 1000.00 $cm^3$ ammonia solution $2 \cdot 3.59 \cdot 10^{-4} = 7.18 \cdot 10^{-4}$ mol ammonia can be found.

| | |
|---|---|
| In 1 mol ammonia | 14.01 g N |
| In $7.18 \cdot 10^{-4}$ mol ammonia | x g N |

$$x = 7.18 \cdot 10^{-4} \cdot 14.01 = 0.0101 \text{ g}$$

*Thus, 0.0101 g of nitrogen can be found in the solution.*

4. For titration of 150.0 mg of analytically pure sodium carbonate sample 30.06 $cm^3$ hydrochloric acid standard solution is consumed. Calculate the exact molarity of the hydrochloric acid standard solution! $M(Na_2CO_3) = 105.99$ g/mol

   The equation that serves as base for the determination:

$$Na_2CO_3 + 2\ HCl = 2\ NaCl + H_2O + CO_2$$

| | |
|---|---|
| 1 mol $Na_2CO_3$ | 105.99 g |
| x mol $Na_2CO_3$ | 0.1500 g |

$$x = \frac{0.1500}{105.99} = 1.42 \cdot 10^{-3}\ mol$$

Because 1 mole sodium carbonate reacts with 2 moles of hydrochloric acid:

| | |
|---|---|
| 30.06 $cm^3$ of hydrochloric acid standard solution | $2.84 \cdot 10^{-3}$ mol HCl |
| 1000.00 $cm^3$ of hydrochloric acid standard solution | x mol HCl |

$$x = \frac{1000.00 \cdot 2.84 \cdot 10^{-3}}{30.06} = 0.0945\,\text{mol}$$

*Thus, the exact concentration of the hydrochloric acid standard solution is 0.0945 M.*

5. 1.0365 g contaminated sodium hydrogen carbonate sample is dissolved in distilled water in a 100.00 $cm^3$ measuring flask. 10.00 $cm^3$ solution is taken out from the flask and it is titrated with 0.1010 M hydrochloric acid. The consumption of the measuring solution was 10.45 $cm^3$. (The contamination does not react with hydrochloric acid.) What was the %-of the pure compound in the contaminated sample? $M(NaHCO_3) = 84.01$ g/mol

The equation that gives the base of the determination:

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$$

| | |
|---|---|
| 1000 $cm^3$ of hydrochloric acid standard solution | 0.1010 mol HCl |
| 10.45 $cm^3$ of hydrochloric acid standard solution | x mol HCl |

$$x = \frac{10.45 \cdot 0.1010}{1000} = 1.055 \cdot 10^{-3}\,mol$$

In the titrated 10.00 $cm^3$ aliquot 0.10365 g $NaHCO_3$ is dissolved.

| | |
|---|---|
| 1 mol $NaHCO_3$ | 84.01 g |
| $1.055 \cdot 10^{-3}$ mol $NaHCO_3$ | x g |

$$x = 1.055 \cdot 10^{-3} \cdot 84.01 = 0.08867 \text{ g}$$

| | |
|---|---|
| 0.10365 g of$NaHCO_3$ | 100 % |
| 0.08867 g of $NaHCO_3$ | x % |

$$x = \frac{0.08867 \cdot 100}{0.10365} = 85.55\%$$

*Thus, 85.55 % percent of the contaminated sample is pure $NaHCO_3$.*

# VIII Complexes

Complexes form one of the biologically most important groups of organic and inorganic compounds. Those substances in which two or more ions or molecules are connected to a central metal ion (or atom) with a coordinative bond are called complex substances. Complex substances are composed of a central metal ion (metal atoms) to which ions or molecules are connected (ligands). The ligands form the so called first coordinate sphere of the central metal ion (atom).

The charge of a complex ion is the sum of charges of the central ion and that of the ligands. If the total charge of the ligands does not compensate the positive charge of the central ion, then the complex is a cation; if the negative charge of the ligands exceeds the positive charge of the central metal ion, then a complex anion is formed. It can occur that the negative charge of the ligands in the first coordinate sphere neutralise the positive charge of the central metal ion (e.g. $[Cr(NH_3)Cl_3]$ complex); or the central metal with a 0 oxidation number forms a complex with neutral ligands. $[Fe(CO)_4]$ is an example of neutral complexes.

The second coordinate sphere can be found outside the first coordinate sphere, which is occupied by completely dissociable electrolytes (ions). The ions of the second coordinate sphere are isolated and hydrated particles in an aqueous solution. For example from an aqueous solution of $[Cr(NH_3)_6]_2(SO_4)_3$, $SO_4^{2-}$ ions can be completely precipitated by barium ions. In contrast, from an aqueous solution of $K[Ag(CN)_2]$, silver ions cannot be precipitated with chloride ions, because practically there are no isolate and hydrated silver ions in the solution.

A special form of complex ions are in which ligands are water molecules. Water molecules, because of their high dipole moment, are very suitable to take part in coordinate bonding. As a result of this bonding, water molecules are interpreted as ligands of aqua complexes. The strength of bonding between different metal ions and water molecules can be different. Alkali metals show a slight tendency for complex formation, in this case bindings are weak. In case of some metal ions (e.g. Fe(III) or Al(III) ), however, these bindings are so strong that water molecules in the second coordinate sphere can accept proton from the complexed water molecules in an acid-base reaction. In such a case, the ligand in the first coordinate sphere remains as a hydroxide ion; in other words the complex hydrolyses. The stability of the aqua complexes might varies from the hydration to the strong bindings.

In stable aqua complexes, formation of complexes with strongly connecting ligands is a ligand exchange reaction; transformation of an aqua complex into another complex. This ligand exchange process is the result of several consecutive steps; exchange of water molecules bonded to the central metal ion occurs through consecutive equilibrium processes:

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5SCN]^{2+} + H_2O$$

$$[Fe(H_2O)_5]^{2+} + SCN^- \rightleftharpoons [Fe(H_2O)_4(SCN)_2]^{+} + H_2O$$

Based on the above interpretations, the strength of connections betwwen the central metal ion and the ligands can be different and the differences can determine the thermodynamic stability of the compounds. If the central metal ion is indicated by M and the ligands by X (the charges are not shown), the consequitive equilibriums of complex formation can be expressed as below:

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$$M + X \rightleftharpoons MX$$

$$MX + X \rightleftharpoons MX_2$$

$$MX_{n-1} + X \rightleftharpoons MX_n$$

The *stability constant*, characteristics of an equilibrium process, can be written to each step of the complex formation reaction:

$$K_1 = \frac{[MX]}{[M]\cdot[X]}$$

$$K_2 = \frac{[MX_2]}{[MX]\cdot[X]}$$

$$K_n = \frac{[MX_n]}{[MX_{n-1}]\cdot[X]}$$

The $K_1$, $K_2$, … $K_n$ values are the stepwise stability constants of a complex, and these numbers are the reciprocal values of the corresponding dissociation constants. In addition to the stepwise stability constants, *cumulative complex stability constants* ($\beta_n$ ) can also be defined:

$$M + nX \rightleftharpoons MX_n$$

$$\beta_n = \frac{[MX_n]}{[M][X]^n}$$

where the $\beta_n$ is *cumulative complex stability constants* ($\beta_n$ ) which can be obtained by multiplication of the *stepwise stability constants* ($K_{1-n}$).

It is an experimental fact that formation of complexes is not an instantaneous process. For understanding this observation, it has to be considered that ligands are not connected to a free central metal ion but they have to replace other ligands (e.g. water molecules), which had already been connected to the central ion. If this exchange is a slow process, the parent complex is kinetically *inert*. If the free ligand exchanges rapidly with the already bonded ligand, the complex is kinetically *labile*.

## VIII.1 Demonstration: Formation of complex salts

Pour 1 $cm^3$ of 0.2 M copper(II) sulphate solution into a test tube and 1 $cm^3$ of 0.5 M nickel(II) sulphate solution into another one. Add concentrated ammonia solution into both test tubes until formation of precipitate can be seen. Note the colours of the precipitates. Then add further amount of ammonia solution to the content of the test tubes until the precipitates dissolve. Note the colours of the solutions.

Interpretation of the experiments:

On addition of ammonia solution hydroxide precipitates are formed in both the copper(II) sulphate and the nickel(II) sulphate solutions:

$$Cu^{2+}_{(aq)} + 2\ OH^- \rightarrow \underline{Cu(OH)_2}$$

$$Ni^{2+}_{(aq)} + 2\ OH^- \rightarrow \underline{Ni(OH)_2}$$

The formed precipitates are dissolved on addition of additional amount of ammonia solution due to formation of ammin complexes:

$$\underline{Cu(OH)_2} + 4\ NH_3 \rightleftharpoons \underset{\text{blue violet}}{[Cu(NH_3)_4]^{2+}} + 2\ OH^-$$

$$\underline{Ni(OH)_2} + 4\ NH_3 \rightleftharpoons \underset{\text{blue}}{[Ni(NH_3)_6]^{2+}} + 2\ OH^-$$

## VIII.2 **Experimental task**

### VIII.2.1 Preparation of tetraammincopper(II) sulphate ($[Cu(NH_3)_4](SO_4)_2 \cdot H_2O$) complex

On addition of aqueous ammonia solution to aqueous solution of copper(II) salts insoluble basic copper salts appear, which can be dissolved on addition of additional amount of ammonia solution (see above). Alcohols decrease solubility of the forming complex salt and dark-blue copper complex is crystalized out on cooling.

Weigh out 5 g of crystalline copper sulphate ($CuSO_4 \cdot 5H_2O$) (previously pulverised in a mortar) on a laboratory balance. Dissolve the weighed crystals in 5 cm$^3$ distilled water and, under the hood, add 7.5 cm$^3$ of concentrated ammonia solution. If light-blue precipitate would remain on the bottom of the glassware, further amount of ammonia has to be added in small portions to dissolve the precipitate. Then add 10 cm$^3$ methanol and place the solution (covered by a watch glass) into ice water for 1-2 hours. The formed dark-blue crystals are to be filtered by a Buchner funnel (connected with a vacuum pump) and washed with small portions of cooled methanol-concentrated ammonia 1:1 (V/V) mixture. Flush the prepared compound with a small portion of cooled methanol and dry it by water pump vacuum. After measuring the mass of the crystals, keep them in a well-sealed bottle.

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## VIII.3 Calculations

1. 5.00 $cm^3$ $1.0 \cdot 10^{-3}$ M copper(II) sulphate solution is added to 20.00 $cm^3$ $5.0 \cdot 10^{-1}$ M ammonia solution. Calculate the concentration of the free copper(II) ion. ($\beta_4 = 2.0 \cdot 10^{12}$ $dm^{12}/mol^4$)

Tetraammincopper(II) complex ion is formed in the reaction:

$$Cu^{2+}{}_{(aq)} + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

The cumulative stability constant of the complex:

$$\beta_4 = \frac{\left[Cu\left(NH_3\right)_4{}^{2+}\right]}{\left[Cu^{2+}\right]\left[NH_3\right]^4}\ \mathrm{dm^{12}/mol^4}$$

With a good approximation $[Cu(NH_3)_4{}^{2+}] = [Cu^{2+}]_{initial,}$ considering almost the whole amount of copper(II) ions is transfomed into the tetraammin complex.

$$[NH_3]_{equilibrium} = [NH_3]_{initial} - [Cu^{2+}]_{initial}$$

In the mixed solution:

$$\left[\mathrm{Cu}^{2+}\right]_{inital} = \frac{\left(5.00 \cdot 1.0 \cdot 10^{-3}\right)}{25.00}\ \mathrm{M;}$$

and

$$\left[\mathrm{NH_3}\right]_{initial} = \frac{\left(20.00 \cdot 5.0 \cdot 10^{-1}\right)}{25.00}\ \mathrm{M}$$

Thus,

$$\left[Cu\left(NH_3\right)_4{}^{2+}\right] = \frac{\left(5.00 \cdot 1.0 \cdot 10^{-3}\right)}{25.00}\ \mathrm{M}$$

$$\beta_4 = 2.0 \cdot 10^{12} = \frac{\dfrac{\left(5.00 \cdot 1.0 \cdot 10^{-3}\right)}{25.00}}{\left[Cu^{2+}\right]\left[\dfrac{\left(20.00 \cdot 5.0 \cdot 10^{-1}\right)}{25.00} - \dfrac{\left(5.00 \cdot 1.0 \cdot 10^{-3}\right)}{25.00}\right]^4}\ \mathrm{dm^{12}/mol^4}$$

$$\left[\mathrm{Cu}^{2+}\right] = \frac{\left(2.0 \cdot 10^{-4}\right)}{2.0 \cdot 10^{12} \cdot \left(4.0 \cdot 10^{-1} - 2.0 \cdot 10^{-4}\right)^4}\ \mathrm{M}$$

Neglecting changes in the initial concentration of ammonia:

$$\left[\mathrm{Cu}^{2+}\right] = \frac{\left(2.0 \cdot 10^{-4}\right)}{2.0 \cdot 10^{12} \cdot \left(4.0 \cdot 10^{-1}\right)^4} = \frac{2.0 \cdot 10^{-4}}{2.0 \cdot 10^{12} \cdot 2.56 \cdot 10^{-2}} = 3.906 \cdot 10^{-15}\ \mathrm{M}$$

*Thus, concentration of the free copper(II) ions in the solution is* $3.9 \cdot 10^{-15}$ *M.*

2. Calculate the concentration of free zinc ions in a solution that is made by mixing 20.00 cm$^3$ of 0.01 M zinc(II) nitrate and 30.00 cm$^3$ of 0.01 M triethylenetetramine solutions. After mixing, the metal to ligand proportion in the formed complex is 1:1. ($\beta = 1.0 \cdot 10^{12}$ dm$^3$/mol)

Reaction of complex formation between zinc ions and triethylenetetramine (TETA) molecules:

$$Zn^{2+} + TETA \rightleftharpoons [Zn(TETA)]^{2+}$$

Concentration of the reactants after mixing the solutions:

$$\left[\mathrm{Zn}^{2+}\right]_{\mathrm{initial}} = \frac{(20{,}00 \cdot 0{,}01)}{50{,}00} = 0.004\,\mathrm{M}$$

$$[\mathrm{TETA}]_{\mathrm{initial}} = \frac{(30{,}00 \cdot 0{,}01)}{50{,}00} = 0.006\,\mathrm{M}$$

Considering that each zinc ion goes into reaction:

$$[\mathrm{TETA}]_{\mathrm{equilibrium}} = 0.002\ \mathrm{M}$$

$$[\mathrm{Zn(TETA)}^{2+}]_{\mathrm{equilibrium}} = 0.004\ \mathrm{M}$$

Based the complex stability constant:

$$\beta = \frac{\left[Zn(TETA)^{2+}\right]}{\left[Zn^{2+}\right][TETA]}\ \mathrm{dm^3/mol}$$

$$10^{12} = \frac{0.004}{\left[Zn^{2+}\right] \cdot 0.002}$$

$$\left[Zn^{2+}\right] = \frac{0.004}{10^{12} \cdot 0.002} = 2 \cdot 10^{-12}\ \mathrm{M}$$

*Thus, concentration of the free zinc ions in the solution is* $2 \cdot 10^{-12}$ *M.*

3. Stability constant of a MY complex is $\beta = 2.0 \cdot 10^3$ dm$^3$/mol. Calculate the concentration of free metal ions if concentration of the complex is $2.0 \cdot 10^{-3}$ M.

Stability constant of the complex:

$$\mathrm{M + Y \rightleftharpoons MY}$$

$$\beta = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{Y}]}$$

The number of metal ions and ligands formed by dissociation of the complex is the same:

$$[\mathrm{M}] = [\mathrm{Y}]$$

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The equilibrium concentration of the complex:

$$[MY]_{equilibrium} = [MY]_{initial} - [M]$$

Accordingly,

$$\beta = \frac{[MY]_{initial} - [M]}{[M]^2}$$

$$2.0 \cdot 10^3 = \frac{2.0 \cdot 10^{-3} - M}{M^2}$$

$$2.0 \cdot 10^3 [M]^2 = 2.0 \cdot 10^{-3} - [M]$$

$$2.0 \cdot 10^3 [M]^2 + M - 2.0 \cdot 10^{-3} = 0$$

$$[M]_{1,2} = \frac{-1 \pm \sqrt{1-\left(4 \cdot 2.0 \cdot 10^3 \cdot \left(-2.0 \cdot 10^{-3}\right)\right)}}{2 \cdot 2.0 \cdot 10^3} = \frac{-1 \pm \sqrt{1+16}}{4.0 \cdot 10^3} = \frac{1 \pm 4.12}{4.0 \cdot 10^3} = \frac{5.12}{4.0 \cdot 10^3} = 1.28 \cdot 10^{-3}$$

*Thus, concentration of the free metal ions is* $1.28 \cdot 10^{-3}$ *M.*

4. Stability constant of a zinc-EDTA (ZnY) complex is $\beta = 3.0 \cdot 10^{16}$ $dm^3$/mol. Concentration of aqueous solution of the complex is $2.0 \cdot 10^{-2}$ M. The ZnY-solution was made in a solvent containing 0.100 M EDTA (Y). Calculate the free zinc ion concentration of the solution!

Reaction of complex formation in solution (charges are not indicated):

$$Zn + Y \rightleftharpoons ZnY$$

Stability constant of the forming complex:

$$\beta = \frac{[ZnY]}{[Zn][Y]}$$

Because the complex salt was dissolved in a 0.100 M EDTA (Y) solution:

$$[Y] = 1.00 \cdot 10^{-1} \text{ M}$$

Accordingly,

$$\beta = 3.0 \cdot 10^{16} = \frac{2.0 \cdot 10^{-2}}{[Zn] \cdot 1.00 \cdot 10^{-1}}$$

$$[Zn] = \frac{2.0 \cdot 10^{-2}}{3.0 \cdot 10^{16} \cdot 1.00 \cdot 10^{-1}} = 6.7 \cdot 10^{-18} \text{ M}$$

*Thus, concentration of the free zinc(II) ions is* $6.7 \cdot 10^{-18}$ *M.*

5. What are the form and equilibrium concentration of the silver ion containing species in a mixture of $1.0 \cdot 10^{-2}$ M silver nitrate and $1.0 \cdot 10^{-1}$ M ammonia solution? ($K_1 = 2.0 \cdot 10^2$ mol/dm$^3$ , $K_2 = 2.0 \cdot 10^7$ mol/dm$^3$)

The complex-forming reactions:

$$Ag^+_{(aq)} + NH_{3(aq)} \rightleftharpoons [Ag(NH_3)]^+_{(aq)}$$

$$[Ag(NH_3)]^+_{(aq)} + NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)}$$

Thus,

$$K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]}$$

$$K_2 = \frac{[Ag(NH_3)_2{}^+]}{[Ag(NH_3)^+][NH_3]}$$

From these expressions:

$$\beta_2 = K_1 \cdot K_2 = \frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$$

$$\beta_2 = 2.0 \cdot 10^2 \cdot 2.0 \cdot 10^7 = 4.0 \cdot 10^9 \ \text{dm}^6/\text{mol}^2$$

Supposing that total amount of silver ions is complexed with the maximal coordination number $[Ag(NH_3)_2]^+$

$$[Ag(NH_3)_2{}^+] = [Ag^+]_{initial}, \text{ and}$$

$$[NH_3] = 1.0 \cdot 10^{-1} - (2.0 \cdot 10^{-2}) = 8.0 \cdot 10^{-2}$$

Concentration of the silver ions:

$$[Ag^+] = \frac{1.0 \cdot 10^{-2}}{4.0 \cdot 10^9 \cdot (8.0 \cdot 10^{-2})^2} = \frac{1.0 \cdot 10^{-2}}{2.56 \cdot 10^7} = 3.91 \cdot 10^{-10} \text{ M}$$

Concentrations of the silver ion containing complex species:

$$[Ag(NH_3)^+] = 2.0 \cdot 10^2 \cdot 3.91 \cdot 10^{-10} \cdot 8.0 \cdot 10^{-2} = 62.56 \cdot 10^{-10} = 6.26 \cdot 10^{-9} \text{ M}$$

$$[Ag(NH_3)_2{}^+] = 2.0 \cdot 10^7 \cdot 3.91 \cdot 10^{-10} \cdot 6.4 \cdot 10^{-3} = 50.05 \cdot 10^{-6} = 5.01 \cdot 10^{-5} \text{ M}$$

*Thus, distribution of silver ions as follows:*

$$[Ag^+] = 3.91 \cdot 10^{-10} \text{ M}$$

$$[Ag(NH_3)^+] = 6.26 \cdot 10^{-9} \text{ M}$$

$$[Ag(NH_3)_2{}^+] = 5.01 \cdot 10^{-5} \text{ M}$$

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# IX Electrochemistry

Electrochemistry encompasses the electrical phenomena based on chemical reactions and the chemical reactions that occur as an effect of electric current. The base of both types of alterations is the electron transfer, i.e. *redox reactions*.

*Redox reactions* (or oxidation-reduction reactions) are reactions that involve a transfer of electrons between species (reactants). *Oxidation* as a part of a redox reaction in which there is a loss of electrons by a species or an increase in the oxidation number of an atom. *Reduction* is the part of a redox reaction in which there is a gain of electrons by a species or a decrease in the oxidation number of an atom. In any reaction in which oxidation occurs, reduction must also occur.

Further characteristics and basis of balancing of redox reactions are discussed in Chapter II.

## IX.1 Electrochemical cells

The common feature of the electric phenomena based on chemical reactions is that spontaneous electron transfer reactions generate an electric current. The direction of the spontaneous redox reactions is determined by relative redox potentials of the redox systems that are involved in the reactions.

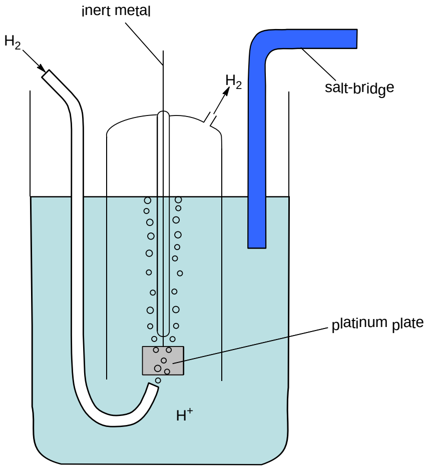
The redox properties of elements can be characterized by their *electrode potential*s derived from the original *Nernst equation*. Electrode potential of a metal at 25 °C can be calculated according the equation as follows:

$$E = E^0 + \frac{0.059}{n}\log c$$

where $E$ = the actual electrode potential (V);
$E_0$ = the standard potential (V);
$n$ = the number of transferred electrons (per particle); and
$c$ = concentration (activity) of the oxidized form of the metal (mol/dm$^3$).

Electrode potentials of elements and that of other kind of reversible redox systems can only be determined by measurements of potential differences. At first, the electrode potentials were determined against the potential of the *standard hydrogen electrode* (Figure IX-1) of which potential was arbitrary set to be zero ($E_0$ = 0.00V). Thus, the potential of any electrode can be obtained by connecting it to the standard hydrogen electrode and measure the electromotive force of the galvanic cell.

**Figure IX-1.** Schematic diagram of the hydrogen electrode



Similar to that of elements, the potential of any other reversible redox system can be experimentally determined. In these sets of experiments an electrochemically inert metal (or graphite) electrode is submerged into a solution containing both oxidized and reduced forms of a reversible redox system and the electrode (called *redox electrode*) is connected to the standard hydrogen electrode.

Redox potentials can be calculated according to the *Nernst* equation, of which form referring to 25 $^{o}$C as it follows:

$$E = E_0 + \frac{0.059}{n}\log\frac{[ox]}{[red]}$$

where

$E$ = the actual electrode potential (V);
$E_0$ = the standard potential (V);
$n$ = the number of transferred electrons (per particle); and
[ox] = concentration (activity) of the oxidized form of the element (mol/dm$^3$).
[red] = = concentration (activity) of the reduced form of the element (mol/dm$^3$).

The direction of flow of electrons in a spontaneous redox reaction can be determined by comparison of the electrode and/or redox potentials of the reversible redox systems ($ox_1/red_1$ and $ox_2/red_2$) of the reactions.

$$ox_1 + red_2 = red_1 + ox_2$$

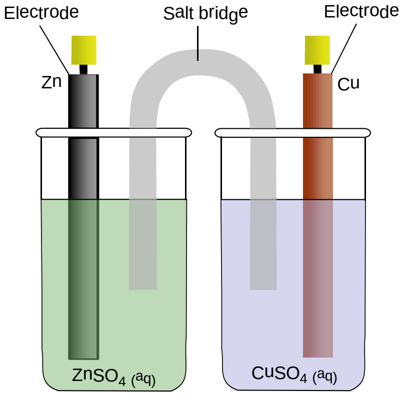
When $E(ox_1/red_1) > E(ox_2/red_2)$ the direction of a spontaneous redox reaction corresponds to the above generalized chemical reaction. In other words, in spontaneous redox reaction the redox system with the more positive standard potential oxidizes the more negative one. The redox system with the more negative standard potential reduces the more positive one.

A *galvanic cell*, or *voltaic cell*, named after *L. Galvani*, or *A. Volta* respectively, is an electrochemical cell that derives electrical energy from *spontaneous redox reaction*s taking place in two half cells. The *Daniell cell* is designed to make use of the spontaneous redox reaction between zinc and copper(II) ions to produce an electric current (Figure IX-2). It consists of two half-cells. The half-cell on the left contains a zinc metal electrode dipped into $ZnSO_4$ solution. The half-cell on the right consists of copper metal electrode in a solution $CuSO_4$. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution and provides matrix for the necessary ion migration.

Comparison of the (reductive) standard electrode potential of the $Zn^{2+}/Zn$ ($E^o$ = -0.76 V) and that of the $Cu^{2+}/Cu$ ($E^o$ = + 0.34 V) indicates that in the spontaneous redox reaction elementary zinc is oxidized an copper(II) ions are reduced. The two reactions occur in form of half-cell reactions. The half-cell (electrode) in which oxidation occurs is called *anode* and that in which reduction takes place is called *cathode*.

anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

**Figure IX-2.** Schematic diagram of the Daniell cell



Cell notations are a shorthand description of voltaic or galvanic (spontaneous) cells. The reaction conditions (pressure, temperature, concentration, etc.), the anode, the cathode, and the electrode components are all described in this unique shorthand. Cell notation rules are as follows:

1. The *anode* half-cell is described first; the *cathode* half-cell follows. Within a given half-cell, the reactants are specified first and the products last. Spectator ions are not included.
2. A single vertical line ( | ) is drawn between two chemical species that are in different phases but in physical contact with each other (e.g., solid electrode | liquid with electrolyte). A double vertical line ( || ) represents a salt bridge or porous membrane separating the individual half-cells.
3. The phase of each chemical (s, l, g, aq) is shown in parentheses. If the electrolytes in the cells are not at standard conditions, concentrations and/or pressure are included in parentheses with the phase notation.

Using the rules above, the notation for the *Daniell cell* is:

Zn | 1 M $ZnSO_4$ solution || 1 M $CuSO_4$ solution |Cu

The *electromotive force* (EMF) of a galvanic cell is the maximum potential difference between two electrodes of a galvanic or voltaic cell. Electromotive force is also known as voltage, and it is measured in volts. It can be calculated as the sum of the oxidation and reduction potentials:

$$EMF = E_{red,cathode} + E_{ox,anode}$$

The electrode (and redox) potentials are uniformly given for the reduction reactions. The oxidation potentials are the negative of standard reduction potentials:

$$E_{ox,anode} = -E_{red,cathode}$$

Accordingly, the electromotive force can also be expressed as the difference of the reduction potential of the cathode and the anode:

$$\mathrm{EMF} = \Delta E = E_{\mathrm{red,cathode}} - E_{\mathrm{red,anode}}$$

Application of the above for the *Daniell cell*:

$$E_{\mathrm{Zn}} = E^0_{\mathrm{Zn^{2+}/Zn}} + \frac{0.059}{2}\log\left[\mathrm{Zn^{2+}}\right], \text{ and}$$

$$E_{\mathrm{Cu}} = E^0_{\mathrm{Cu^{2+}/Cu}} + \frac{0.059}{2}\log\left[\mathrm{Cu^{2+}}\right]$$

where

$E^0_{\mathrm{Zn}}$ = the actual redox potential of the zinc electrode (V)

$E^0_{\mathrm{Cn}}$ = the actual redox potential of the copper electrode (V)

$E^0_{\mathrm{Zn^{2+}/Zn}}$ = the (reduction) standard potential of the zinc electrode ($E^0_{\mathrm{Zn^{2+}/Zn}}$ = -0.76 V)

$E^0_{\mathrm{Cu^{2+}/Cu}}$ = the (reduction) standard potential of the copper electrode ($E^0_{\mathrm{Cu^{2+}/Cu}}$ = +0.34 V).

Considering that both electrodes are standard electrodes (i.e., $[\mathrm{Zn^{2+}}] = [\mathrm{Cu^{2+}}]$ = 1.0 M), the EMF can be calculated as follows:

$$\mathrm{EMF} = E_{\mathrm{Cu^{2+}/Cu}} - E_{\mathrm{Zn^{2+}/Zn}}$$

$$\mathrm{EMF} = +0.35\ \mathrm{V} - (-0.76\ \mathrm{V}) = +1.10\ \mathrm{V}$$

Thus, the electromotive force (EMF) of the galvanic cell constructed from standard zinc and standard copper electrodes equals +1.10 V. In the half-cells zinc is oxidized and copper ions are reduced.

## IX.2 Electrochemical pH measurement

Precise determination of hydrogen ion concentration (pH) of aqueous solutions is frequent task in chemical laboratories. Such determinations can be performed on the basis of concentration dependence of the electrode potentials (*Nernst equation*).

According to the *Nernst* equation potential of a hydrogen electrode depends on the solution's hydrogen ion (oxonium ion) concentration (activity) as follows:

$$E = E^{0}_{\mathrm{H^+}/H_2} + \frac{0.059}{1}\log[\mathrm{H^+}]$$

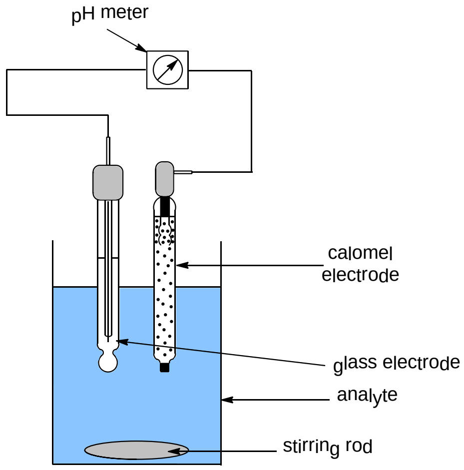
where

$E$ = the actual potential of the hydrogen electrode (V)
$E^0$ = the standard potential of the hydrogen electrode (V)
$[H^+]$ = hydrogen ion (oxonium ion) concentration (activity) (mol/dm$^3$).

Since the absolute potential of an electrode cannot be measured, it should be connected to a *reference electrode* via a salt bridge and the electromotive force (EMF) of the resulting galvanic cell is measured. The classical reference electrode is the standard hydrogen electrode. Because of the unfavourable practical properties of this electrode, in practice it is replaced by *electrodes of second kind* (e.g., calomel electrode ($Hg/Hg_2Cl_2$), or Ag/AgCl-electrode) which are slightly polarizable and have constant, reproducible potentials.

Because of practical difficulties of the hydrogen electrodes, hydrogen ion concentrations are determined – almost exclusively - by so called *ion selective membrane electrodes*. Reversible ion selective membrane electrodes can also be used to determine several other cations (e.g., $K^+$, $Na^+$, $Ca^{2+}$) and anions (e.g., $Cl^-$, $Br^-$ $I^-$). The most widely used hydrogen ion selective membrane electrode is the *glass electrode* (Figure IX-4.). Accordingly, if a glass electrode is immersed into a solution containing hydrogen ions, the potential of the glass electrode will be proportional to the concentration of hydrogen ions in the solution. Consequently, if a glass electrode and a reference electrode are immersed into an acid or an alkaline solution, the EMF of the cell will be proportional to the pH of the solution (Figure IX-3). Recently, so called combined glass electrodes are used in which the reference electrode is also built in (Figure IX-5.).

**Figure IX-3.** Potentiometric pH measurement

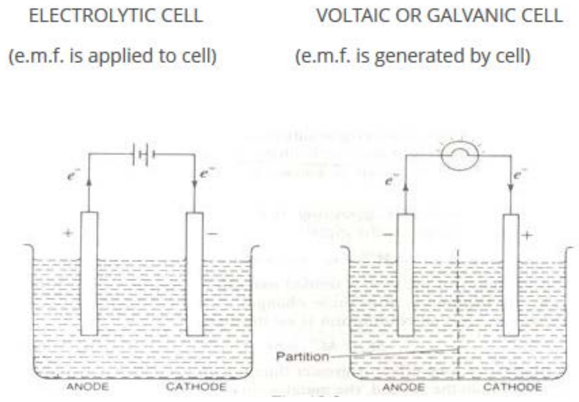


## IX.3 Electrolysis

*Electrolysis* is a method of using a direct electric current to drive an otherwise non-spontaneous chemical (redox) reaction. Electrolysis is carried out in an *electrolytic cell*. The electrolytic cell involves submerging two metal (or graphite) electrodes into a liquid or molten substance that contains positive and negative ions. The electrodes are connected to a battery. When they are electrically charged, one electrode becomes the negative terminal or *cathode*, and the other becomes the positive terminal or *anode*. The positive terminal attracts negatively charged ions and the negative terminal attracts positively charged ions.

Once a *critical voltage* level (decomposition voltage) is exceeded, electrolysis reaction proceeds at a rate determined largely by the current. During electrolysis, ions with a positive electrical charge move toward the cathode (negative pole), where they take up electrons; ions with a negative charge move toward the anode (positive pole), where they give up electrons. Note that the signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells (Figure IX-4).

**Figure IX-4.** Signs of the anode and cathode in galvanic and the electrolytic cells.



When molten salts are electrolyzed metal ions are reduced at the cathode. In case of electrolysis of aqueous solutions water may also be reduced or oxidized at the electrodes. Using appropriate voltage level, water can be reduced to form elementary hydrogen and can be oxidized to form elementary oxygen. In general, simple anions (e.g., chloride, bromide) are oxidized at the anode. When the aqueous solution contains complex anions (e.g., sulphate, nitrate) water is oxidized.

The quantitative aspects of the electrolytic processes can be characterized by *Faraday's' laws*. *Faraday's first law* states that the amount of chemical change that takes place in a solution during electrolysis is directly proportional to the amount of charge passed through the solution:

$$m = k \cdot I \cdot t$$

where,

$m$ = amounts of the substances consumed or produced
$k$ = electrochemical equivalent weight
$I$ = intensity of current (Ampere)
$t$ = time (second)

*Faraday's second law* states that electrochemical transformation of 1 mole ion with charge *z* requires z ·96500 C electric charges. Accordingly, the electric charge ($Q$) needed is directly proportional to the number of moles (n) and the charge (z) of the ion

$$Q = z \cdot n \cdot F$$

where

$F$ = 96500 C/mol (*Faraday constant*)

By combination of the two laws the *electrochemical equivalent weight* ($k$) of a substance can be calculated:

$$m = \frac{M}{z \cdot F} \cdot I \cdot t$$

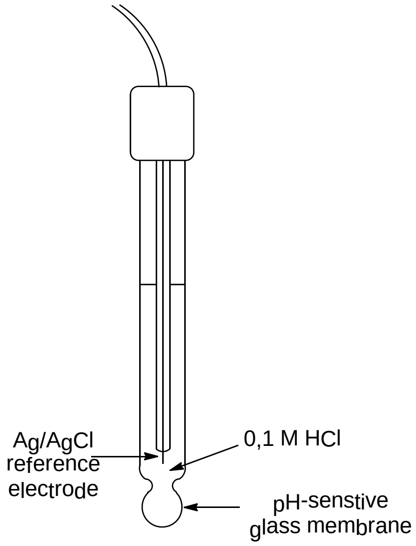
$$k = \frac{M}{z \cdot F}$$

The electrochemical equivalent weight of a substance is that amount of the substance that is electrochemically transformed by 1 coulomb ($C$) charge.

## IX.4 Demonstration: Determination of pH by direct potentiometry

Direct potentiometric measurements are performed using combined glass electrodes (Figure IX-5.). The combined glass electrode is a tube within a tube. The inner tube contains a $1.0\times10^{-7}$ mol/dm$^3$ HCl solution. Also inside the inner tube is the reference electrode (usually silver chloride electrode or calomel electrode). The measuring part of the electrode, the glass bulb on the bottom, is coated both inside and out with a ~10 nm layer of a hydrated gel. These two layers are separated by a layer of dry glass. It is the hydrated gel, which makes the pH electrode an ion-selective electrode.

**Figure IX-5.** Combined glass electrode



Before switching on the instrument, make sure the electrode is immersed into distilled water! A “dry” electrode does not function properly. The re-equilibration of the membrane requires several hours and the lifetime of the electrode would be shorter.

## Calibration

Prior to use, the instrument should be calibrated. For this purpose, two buffer solutions of different, known pH are used. The electrode is removed from distilled water and carefully wiped with a filter paper for removal of adhered water (to avoid uncontrolled dilution of the test solution). Then, the electrode is immersed into the first buffer solution of pH about 7. The electrode should be immersed as deep as the ceramic filter is sunk. The ON/OFF button is pressed and after about one minute pause the nominal pH value of the calibration buffer is adjusted with the STD button. The ON/OFF button is pressed again. The electrode is removed from the solution, rinsed thoroughly with distilled water and dried as described above. Then, the electrode is immersed into the second calibration buffer of about pH 9. The instrument is switched on and – similar to the above – the pH is adjusted with the STD2 button. The electrode is removed from the solution, rinsed and put into distilled water. Thus, the instrument is calibrated.

## Determination of pH of unknown solution

The measurement can be performed after calibration of the instrument. The electrode is rinsed thoroughly with distilled water and dried wiping with a piece of filter paper. Then, the electrode is immersed into the unknown solution and the READ button is pressed. After about a minute (the time needed for equilibration) the stabilized displayed value is recorded. The electrode is rinsed again and immersed again into distilled water. After measurement, the instrument is turned off; the electrode is rinsed with distilled water, wiped with a piece of filter paper and kept it in a 3 M potassium chloride solution till the next measurement.

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## IX.5 Calculations

1. Calculate the electromotive force of the following galvanic cell (t = 25 $^{o}$C): Zn | 0.15 mol/dm$^3$ $ZnSO_4$ solution || 0.32 mol/dm$^3$ $CuSO_4$ solution |Cu? Which electrode is the positive pole (cathode) of the cell? ($E^0_{\mathrm{Cu}}$ = +0.34 V; $E^0_{\mathrm{Zn}}$ = –0.76 V.)

The potential of the copper electrode:

$$E_{\mathrm{Cu}} = E^0_{\mathrm{Cu}} + \frac{0.059}{2} \cdot \log \left[\mathrm{Cu}^{2+}\right]$$

$$E_{\mathrm{Cu}} = +0.34 + \frac{0.059}{2} \cdot \log \left[\mathrm{Cu}^{2+}\right]$$

$$E_{\mathrm{Cu}} = +0.34 + (-0.0146) = +0.325\ \mathrm{V}$$

The potential of the copper electrode:

$$E_{\mathrm{Zn}} = E^0_{\mathrm{Zn}} + \frac{0.059}{2} \cdot \log \left[\mathrm{Zn}^{2+}\right]$$

$$E_{\mathrm{Zn}} = -0.76 + \frac{0.059}{2} \cdot \log 0{,}15$$

$$E_{\mathrm{Zn}} = -0.76 + (-0.0243) = -0.784\ \mathrm{V}$$

The electromotive force of the cell:

$$EMF = E_{\mathrm{Cu}} - E_{\mathrm{Zn}} = +0.325 - (-\ 0.784) = +1.11\ \mathrm{V}$$

*Thus, electromotive force (EMF) of the galvanic cell is 1.11 V. The positive pole (cathode) is the copper electrode.*

2. Calculate the redox potential of the redox electrode in which the concentration of iron(II) sulphate is 0.70 M and that of iron(II) sulphate is 0.30 M. ( $E^0_{\mathrm{Fe(III)/Fe(II)}}$ = +0.77 V )

The potential of a redox electrode:

$$E = E^0 + \frac{0.0591}{z} \cdot \log \frac{[\mathrm{ox}]}{[\mathrm{red}]}$$

$E$ = redox potential
$E^{o}$= standard potential
[ox] = concentration of the oxidized form = [$Fe^{3+}$]
[red] = concentration of the reduced form = [$Fe^{2+}$]
z: the number of transferred electrons (per particle)

$$\mathrm{Fe}^{3+} + \mathrm{e}^- = \mathrm{Fe}^{2+}$$

$$E = +0.77\ \mathrm{V} + 0.0591 \cdot \log \frac{0.70}{0.30} = +0.79\ \mathrm{V}$$

*Thus, redox potential of the $Fe^{3+}$ / $Fe^{2+}$ redox electrode is +0.79 V.*

3. Calculate the electromotive force of the following galvanic cell: $H_2$(Pt) | 0.010 M acetic acid || 1.00 M acetic acid |$H_2$(Pt)? Which electrode is the negative pole (anode) of the cell? ($K_a$ (acetic acid) = $1.85\cdot10^{-5}$ mol/dm$^3$.)

The galvanic cell is a hydrogen electrode concentration cell of which electromotive force (*EMF*) can be calculated as follows:

$$\mathrm{EMF} = +0.059\cdot\log\frac{[\mathrm{H}^+]_1}{[\mathrm{H}^+]_2} \qquad\qquad [\mathrm{H}^+]_1 > [\mathrm{H}^+]_2$$

The hydrogen ion concentration of the acetic acid solutions can be calculated as follows:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[H^+]\cdot[CH_3COO^-]}{[CH_3COOH]} \qquad\qquad [CH_3COO^-] = [H^+] = x$$

$$K_a = \frac{x^2}{[CH_3COOH]}$$

$$x = \sqrt{K_a\cdot[CH_3COOH]}$$

$$0.01\ \mathrm{M}\ CH_3COOH\ :\ [H^+] = \sqrt{1.85\cdot10^{-5}\cdot1.0\cdot10^{-2}} = 4.3\cdot10^{-4}\ \mathrm{M}$$

$$1\ \mathrm{M}\ CH_3COOH\ :\ [H^+] = \sqrt{1.85\cdot10^{-5}\cdot1.00} = 4.3\cdot10^{-3}\ \mathrm{M}$$

$$\mathrm{EMF} = +0.059\cdot\log\frac{4.3\cdot10^{-3}}{4.3\cdot10^{-4}} = +0.059\ \mathrm{V}$$

*Thus, electromotive force of the galvanic (concentration) cell is +0.06 V. The negative pole is the hydrogen electrode with the more diluted acetic acid solution.*

4. A $CuCl_2$ solution is electrolysed between platinum electrodes. Calculate the amount of copper (in grams) and the volume of chlorine gas (in dm$^3$) formed when 19300 coulombs electric charge passed through the solution. Calculate the volume of the gas under normal conditions.

$$\begin{array}{ll} \text{96500 coulomb} & \dfrac{63.5}{2}\ \text{g copper} \\ \text{19300 coulomb} & x\ \text{g copper} \\ \hline \multicolumn{2}{c}{96500 : 19300 = 63.5/2 : x} \end{array}$$

$$x = \frac{63.5\cdot19300}{2\cdot96500} = 6.35\ \text{g copper}$$

$$\begin{array}{ll} 96500\ \text{coulomb} & \frac{22.41}{2}\ \text{dm}^3\ Cl_2\ \text{gas} \\ 19300\ \text{coulomb} & x\text{dm}^3\ Cl_2\ \text{gas} \\ \hline \multicolumn{2}{c}{96500 : 19300 = 22.41/2 : x} \end{array}$$

$$x= \frac{22.41 \cdot 19300}{2 \cdot 96500} =2.24\ \text{dm}^3\ Cl_2$$

*As a result, 2.24 dm$^3$ $Cl_2$ gas is formed at the positive pole and 6.35 g copper is deposited at the negative pole.*

5. 200.0 g of 10.0 m/m% solution of copper(II) sulphate is electrolysed using graphite electrodes. As a result of the electrolytic process 800.0 cm$^3$ of oxygen gas of standard conditions is produced. Calculate the m/m% concentration of the solution at the end of electrolysis. The volume of gases under standard conditions is 24.47 dm$^3$. (M(Cu)=63.55 g/mol; M($O_2$)=32.00 g/mol; M($CuSO_4$)=159.61 g/mol; M($H_2SO_4$)=98.08 g/mol.)

The reactions at the cathode and the anode as follows:
cathode: $Cu^{2+} + 2e^- = Cu$
anode : $H_2O = ½\ O_2 + 2\ H^+ + 2\ e^-$

The copper sulphate content of 200.0 g 10.0 m/m% $CuSO_4$ solution is 20.0 g, which is equivalent to 20.0/63.55 = 0.125 mol.

The amount of 800.0 cm$^3$ $O_2$ under standard conditions:

$$\begin{array}{ll} 1\ \text{mol}\ O_2 & 24.47\ \text{dm}^3 \\ x\ \text{mol}\ O_2 & 0.80\ \text{dm}^3 \\ \hline \multicolumn{2}{c}{x = 0.80/24.47 = 0.0327\ \text{mol}} \end{array}$$

According to the above stoichiometry:

Parallel to production of 0.0327 mol of $O_2$ 2 ·0.0327 = 0.0654 mol of copper(II) ions are reduced to elementary copper. Thus, the amount of copper(II) ions left in the solution is:

$$n(Cu^{2+}) = 0.1253 - 0.0654 = 0.0599\ \text{mol}$$

$$m(CuSO_4) = 0.0599\ \text{mol} \cdot 159.61\ \text{g/mol} = 9.56\ \text{g}$$

The mass of original solutions is reduced because

0.0327 mol of $O_2$ is produced: $m(O_2) = 0.0327\ \text{mol} \cdot 32.00\ \text{g/mol} = 1.05\ \text{g}$, and

0.0654 mol of Cu is produced $m(Cu) = 0.0654\ \text{mol} \cdot 63.55\ \text{g/mol} = 4.16\ \text{g}$

The mass of the obtained solution: $m(\text{solution}) = 200 - (1.05 + 4.16) = 194.79\ \text{g}$

The mass of $CuSO_4$ left in the solution : $m(CuSO_4) = 9.58\ \text{g}$

The m/m% concentration of the obtained solution:

$$\mathrm{m/m}\,\% = \frac{9.58 \cdot 100}{194.80} = 4.92$$

*Thus, concentration of the solution at the end of electrolysis is 4.92 m/m%.*

6. The electromotive force of a galvanic cell consisting of a tin/tin(II) chloride electrode and a standard hydrogen electrode is +0.30 V. Calculate the tin(II) chloride concentration of the solution? ($E^0_{\mathrm{Sn(II)/Sn}}$ = -0.14 V )
7. Calculate the electromotive force of the following galvanic (concentration) cell: $H_2$(Pt) | 0.05 M acetic acid || 0.20 M hydrochloric acid |$H_2$(Pt). Which electrode is the negative pole (anode) of the cell? ($K_a$ (acetic acid) = $1.85 \cdot 10^{-5}$ mol/dm$^3$.)
8. Calculate the electromotive force of the following galvanic (concentration) cell: Ag | 0.02 M silver nitrate solution || 0.40 M silver nitrate solution |Ag.
9. Calculate the electromotive force of the following galvanic (concentration) cell: $H_2$(Pt) | 0.50 M ammonia solution || solution of unknown pH |$H_2$(Pt). The electromotive force of the galvanic cell is +0.30 V. Calculate the pH of the unknown solution. ($K_b$ (ammonia) = $1.79 \cdot 10^{-5}$ mol/dm$^3$.)
10. The electromotive force of the a Zn | $1.0 \cdot 10^{-3}$ M $ZnSO_4$ || 0.10 M $ZnSO_4$ | Zn galvanic (concentration) cell is +0.039 V. Calculate the degree the dissociation of the 0.10 M $ZnSO_4$ solution. The degree of dissociation of the $1.0 \cdot 10^{-3}$ M $ZnSO_4$ solution is considered to be 100%.
11. Calculate the solubility constant of AgCl if the electromotive force of the Ag | saturated AgCl || 0.1M $AgNO_3$ solution | Ag galvanic (concentration) cell is +0.23 V.
12. The electrode potential of the Pb | saturated $PbF_2$ + NaF || is -0.35 V. Calculate the solubility product of $PbF_2$ if $[F^-]$ = 1.0 M.
13. Calculate the electrochemical equivalent weight (*k*) for the aluminium(III), iron(II), iron(III) and sodium ions.
14. Molten sodium chloride is electrolysed with 2.00 A current for 5 hours. Calculate the mass of the deposited metal if the electrochemical percent yield is 85%. M(Na)= 22.99 g/mol
15. A dilute solution of sodium hydroxide is electrolysed with 1.70 A current for 15.0 minutes. Calculate the volume of the formed gases at 25 °C temperature and 93.4 kPa pressure. Calculate the concentration of the solution at the end of electrolysis.

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